Predicting the Distribution Coefficient of Solvent Extraction of Rare Earth Elements Based on the Gibbs Free Energy and Thermodynamic Theory for Equilibrium Constant

A Thesis Submitted to the College of

Graduate and Postdoctoral Studies

In Partial Fulfillment of the Requirements

For the Degree of

Master of Science

In the Department of Chemical and Biological Engineering

University of Saskatchewan

Saskatoon, SK, Canada

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ABSTRACT

Rare Earth Elements (REEs) are a class of 17 elements, including the lanthanides (15 elements), scandium (1 element), and yttrium (1 element). REEs minerals consist of 9-10 REEs excluding promethium. The separation of REEs minerals into their components is achieved by the solvent extraction process, consisting of the organic phase and aqueous phase. Leaching is a process by which REEs are dissolved in acid. The final product of the leaching process (leachate) is sent to the solvent extraction process. The leachate and extractant are mixed well with diluents and left until it produces the two phases. The distribution of REE between these two phases is determined by the distribution coefficient and depends on extractant type, pH, temperature, extractant concentration, diluent type, and diluent concentration. A typical REEs solvent extraction process consists of several stages and is determined by the separation factor of REEs. The separation factor for a binary mixture of REE1 and REE2 is the ratio of the composition of REE1 and REE2. The distribution coefficient is used to determine the separation factor and extraction efficiency.

The intercept difference between two adjacent lanthanides in log D vs. pH plot was analyzed to propose a model. The mean value of the intercept difference between two adjacent lanthanides was determined by using experimental results. The ionic radius of lanthanides deviates linearly according to their atomic number. However, the yttrium position based on the ionic radius is between holmium and erbium. Many experimental results revealed that the intercept position of yttrium in log D vs. pH plot was between holmium and erbium. Based on the mean value difference of two adjacent lanthanides and yttrium's position, a model was proposed to determine the lines of the entire REEs series except for scandium in log D vs. pH plot. It was found that the proposed model can be applied to the log D vs. log (H_2R_2) plot. The theoretical background for REEs deviation in log D vs. pH plot is the standard Gibbs free energy that gradual changes with its atomic number. The proposed model can be utilized to calculate the separation factor of the lanthanides and yttrium. A model was presented to determine any lanthanide extraction efficiency with the aid of the extraction efficiency value of another lanthanide. The present study discusses the theoretical background of the separation factor and the extraction efficiency of two lanthanides.

The model performance was tested with various intercept values of REEs in the log D vs. pH plot and log D vs. log(H_2R_2) plot. It was found that experimental results deviate from the proposed model with reasonable errors. The proposed model can be used to calculate the separation factor

of REEs. However, the model is only valid for a specific range of extractant concentrations and pH from 2 to 4.

ACKNOWLEDGEMENT

First and foremost, I would like to thank my supervisor, Professor Shafiq Alam, for providing me this opportunity to study at the University of Saskatchewan. Also, I would like to thank my graduate advisory committee chair Professor Oon-Doo Baik and committee member Professor Akindele G. Odeshi. Special thanks to my fellow graduate students Olatunji Olabiyi, and Afolabi Ayeni for their support for my research. Finally, my sincere gratitude goes to my two brothers for their supports which motivated me along the way.

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DEDICATION

To my parents, my brothers Nadheera, and Chameera.

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NOMENCLATURE

Symbol	Description
$C_{Aqueous}$	Metal concentration of the aqueous phase
C_{Feed}	Metal concentration of the feed
$C_{H_2R_2}$	The intercept of log D vs log (H_2R_2) plot
C_{pH}	The intercept of log D vs pH plot
C_T	The intercept of log D vs 1/T plot
D	The distribution coefficient
E	Extraction efficiency
$GRD_{H_2R_2}$	The gradient of log D vs log (H_2R_2) plot
GRD_{pH}	The gradient of log D vs pH plot
GRD_T	The gradient of log D vs 1/T plot
H_2R_2	Organic extractant
$M_{Aqueous}$	Molarity of the aqueous phase
$M_{Organic}$	Molarity of the organic phase
N/A	Not available
$n^/$	Number of positive ions in rare earth element
K_{ex}	Equilibrium constant
Ln	Lanthanides
Q	The fluctuations between experimental log D values and estimated log D values
R	Universal gas constant (8.314 J/K.mol)
R^2	Regression coefficient
T	Temperature (K)
t	Time (min)
U	The fluctuations of estimated log D values and the mean of experimental log D values
$V_{Aqueous}$	Volume of the aqueous phase
$V_{Organic}$	Volume of the organic phase

Z	Atomic number
$\alpha(REE_1, REE_2)$	The separation factor between rare earth element 1 and rare earth element 2
ΔG^o	Standard gibs free energy of formation (kJ/mol)
ΔH^o	Standard enthalpy of formation (kJ/mol)
ΔS^o	Standard entropy of formation (J/mol.K)
μ	Mean
σ	The standard deviation
(H_2R_2)	Extractant Concentration (mol/dm^3)

LIST OF ABBREVIATIONS

Symbol	Description
Alimine 308	tri-isooctyl amine
Alimine 336	tri-Octyl/dodecyl
Aliquat 336	tri-octyl methyl ammonium chloride
Cyanex 272	di-2,4,4-trimethylpentylphosphinic acid
Cyanex 301	di-2,4,4-trimethylpentyl-dithiophosphinic acid
Cyanex 302	di-2,4,4-trimethylpentyl-monothiophosphinic acid
Cyanex 923	trialkyl phosphine oxides
D2EHPA	di-2-ethylhexylphosphoric acid
EHEHPA	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
HDEHP	bis-(2-ethylhexyl)
HEHAMP	2-ethylhexylamino) methyl
HEHAPP	2-ethylhexyl-3-(2-ethylhexylamino) pentan-3-yl
HEHEHP	2-ethylhexyl ester
HREE	Heavy Rare Earth Element
HYY-2	di-(2,3-dimethylbutyl) phosphinic acid
ICP-AES	Inductively Coupled Plasma-Atomic Emission Microscopy
IUPAC	International Union of Pure and Applied Chemistry
LED	light-emitting diodes
LREE	Light Rare Earth Element
P204	di-(2-ethylhexyl) phosphoric acid
P227	di-(2-ethylhexyl) phosphinic acid
PR	Phase Ratio
Kr	Krypton
REE	Rare Earth Element
REE1	Rare Earth Element 1
REE2	Rare Earth Element 2
REO	Rare Earth Oxide

TBP	tri-n-butyl-phosphate
TEHA	tri 2-ethylhexyl amine
TODGA	N, N, N’, N’-tetra(n-octyl) diglycolamides
TOPO	tri-n-octyl phosphine oxide
Xe	Xenon

CHAPTER 1

INTRODUCTION AND RESEARCH OVERVIEW

1.1 Introduction

The lanthanides (atomic numbers (Z) 57-71), yttrium (Z=39), and scandium (Z=21) are classified as rare earth elements (REEs) (Charalampides, Vatalis, & Apostoplos, 2015)(Turpeinen et al., 2019). Because yttrium and scandium can be found where lanthanides are available, they are included in the REEs group (Turpeinen et al., 2019). They all share similar chemical properties (Dutta et al., 2016). REEs are gaining attention because of their role in catalysts, rechargeable batteries, and polishing powders (Rabatho, Tongamp, Takasaki, Haga, & Shibayama, 2013)(Dvořák & Vu, 2015)(K. Wang et al., 2017)(Zeng & Cheng, 2009). Notable rare earth minerals such as Basanites, Xenotime, and Monazite contain REEs in different percentages (Xie, Zhang, Dreisinger, & Doyle, 2014).

The hydrometallurgical process is used to separate rare earth minerals into their components (Sprecher et al., 2014). That separation requires a complex system (Yeong, Lee, Lee, Jo, & Whan, 2016)(Y. G. Wang, Xiong, Meng, & Li, 2004) and is achieved by separation techniques such as

solvent extraction, ion exchange, and precipitation (Abreu & Morais, 2014). The latter being used by most industrial REEs separation processes. The solvent extraction process uses leachate as its feed, which is the solution achieved after the filtration of acid leaching (Swain & Mishra, 2019). Active experiments are being carried out to make the process more efficient, economical, and environmentally friendly due to the high demand for REEs throughout the world (Jha et al., 2016).

A typical solvent extraction process consists of two phases, namely the organic phase, and the aqueous phase (leachate). The REEs in the leachate are moved from the leachate to the organic phase in which the REEs are formed complexes with extractants (Quinn, Soldenhoff, Stevens, & Lengkeek, 2015). The formed complexes are dependant on extractant type, extractant concentration, pH, and phase ratio (Knyaz'kina, Kuznetsova, Travkin, Vol'dman, & Glubokov, 2010). Many solvent extractants have been proposed for the REEs separation process. Among these, acidic extractants such as Cyanex 272 (bis-2,4,4-trimethylpentyl phosphonic acid), D2EHPA (di-2-ethylhexylphosphoric acid), and Versatic 10 are well known to extract REEs (Jha et al., 2016). Several studies were carried out on the extraction equilibrium for one or more REEs with Cyanex 272 (Quinn et al., 2015)(K.-A. Li & Freiser, 1986)(Komatsu & Freiser, 1989)(Inaba, Muralidharan, & Freiser, 1993)(L. I. Deqian, 2017), Cyanex 572 (Quinn et al., 2015)(Y. Wang, Li, Zhao, Dong, & Sun, 2015), D2EHEPA (Ohto et al., 1995)(Chen, Li, Chen, Li, & Liu, 2020), EHEHPA (Ohto et al., 1995)(Registered, Street, Kubota, Goto, & Nakashio, 2007), EHEPA (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) (Quinn et al., 2015), Cyanex 272 + TOPO (Komatsu & Freiser, 1989), TBDGA (D. F. Peppard, Mason, Driscoll, & Sironen, 1958), DNPP (Anitha, Kotekar, Singh, Vijayalakshmi, & Singh, 2014), HEHAMP+HEHEMP (Q. Zhao et al., 2019), HL4 (Y. Lu & Liao, 2016), HEHAPP (2-ethylhexyl-3-(2-ethylhexylamino)pentan-3-yl) (Kuang, Zhang, Li, Wei, & Liao, 2018), Cekatonic (Singh, Singh, & Mathur, 2006), Neo heptanol (Singh et al., 2006), Cyanex 301 (di-2,4,4-trimethylpentyl-dithiophosphinic acid) +Cyanex 923 (M. L. P. Reddy, Bharathi, Peter, & Ramamohan, 1999), HEDHP+HEH/EHP (Zhang et al., 2008), and P227 (Chen et al., 2020).

The trivalent form is common for most REEs. Nevertheless, cerium and europium can be found in different valance states such as divalent and tetravalent (Barrat et al., 2020). REEs consist of slight variations in thermodynamic properties such as standard enthalpy of formation, standard Gibbs free energy of formation, and standard entropy of formation (Navrotsky et al., 2015). Moreover,

the lanthanides's trivalent ionic radius reduces with the increase in their atomic number (Pereira et al., 2019). The trivalent ionic radius of yttrium is in between holmium and erbium (Voncken, 2016). Based on the electronic configuration, REEs are categorized into two groups: LREEs (light rare earth elements) and HREEs (heavy rare earth elements) (Pereira et al., 2019).

The distribution of REEs among the aqueous phase (leachate) and the organic phase is determined by the distribution coefficient (Anti et al., 1996). A typical rare-earth mineral contains at least 9-10 REEs (Manis Kumar et al., 2016). The separation factor is applied to calculate the ratio of separation a mixture of two REEs. The distribution coefficient is used to obtain the separation factor and extraction efficiency (Kashi, Habibpour, Gorzin, & Maleki, 2018). The most important parameter to layout a solvent extraction process to separate a mixture of REEs is the distribution coefficient (Williams-wynn, Naidoo, & Ramjugernath, 2020). It was found that many studies investigated the distribution coefficients of one or many REEs through experiments (Nasab, Sam, & Milani, 2011)(Jia et al., 2009)(Tong et al., 2009)(Wei, Li, Zhang, & Liao, 2019)(S. Wu et al., 2017). Nevertheless, a numerical study for the solvent of REEs emphasizes that the distribution coefficient has not been carried out. The present study focuses on proposing a model for the quantitative prediction of the entire REE series distribution coefficients.

1.2 Knowledge Gaps

I. Although many studies focus on the experimental determination of the distribution coefficient, a numerical analysis was not carried out on the distribution coefficient behaviour with REEs.
II. Many experimental findings show that REEs lines in log D vs pH are parallel to each other. Moreover, the intercepts of the lanthanides increase with its increasing atomic number.
III. As mentioned above, the relationship between lanthanides atomic number and intercept in log D vs pH plot is found in log D vs log(H_2R_2) plot. Nevertheless, there is no explanation regarding the theoretical background behind this behaviour.

1.3 Hypothesis

I. The intercepts of the lanthanides in log D vs. pH plot deviate gradually according to their atomic number.

II. The nature (structure, and number of components) of the formed complex in the REEs solvent extraction process relies on extractant concentration, extractant type, pH, and the number of extractants.

III. In the lanthanides, the relationship between atomic number and the trivalent form's ionic radius is linear.

1.4 Objectives

The main goal of this research project is to propose a model to predict the distribution coefficient of REEs solvent extraction.

I. To carry out a statistical analysis for available experimental results of the intercept difference between two adjacent REEs in log D vs. pH plot.

II. To propose a model to predict the entire REE series distribution coefficient in log D vs. pH plot.

III. To find the theoretical background behind the intercept difference between two adjacent REEs in log D vs. pH, and log D vs. log (H_2R_2).

IV. To determine the separation factor based on the intercept difference between two adjacent REEs.

V. To analyze existence of any relationship between the extraction efficiency of two adjacent REEs based on their distribution coefficient development.

CHAPTER 2

LITERATURE REVIEW

2.1 The Rare Earth Elements

The term rare earth elements (REEs) is used to describe a group of elements that contain yttrium, scandium, and the fifteen lanthanides elements: lanthanum (La), yttrium (Y), cerium (Ce), ytterbium (Yb), praseodymium (Pr), erbium (Er), neodymium (Nd), samarium (Sm), dysprosium (Dy), europium (Er), gadolinium (Gd), promethium (Pm), terbium (Tb), holmium (Ho), thulium (Tm), lutetium (Lu), and scandium (Sc). There are 17 elements in the REEs group (Figure 2.1) (W. Wang, Pranolo, & Cheng, 2011). The REEs are divided into two groups based on their atomic number: Light REEs (Z: from 57 to 63) and Heavy REEs (Z: from 64 to 71). Even though REEs are considered rare, they are plentiful in the environment. However, REEs are often dispersed in the environment because of their geochemical properties; for example, the 25th abundant element, cerium is more abundant than copper (Migaszewski & Gałuszka, 2015). The atomic number deviation of REEs are given in Table 2.1 (Aide & Aide, 2012).

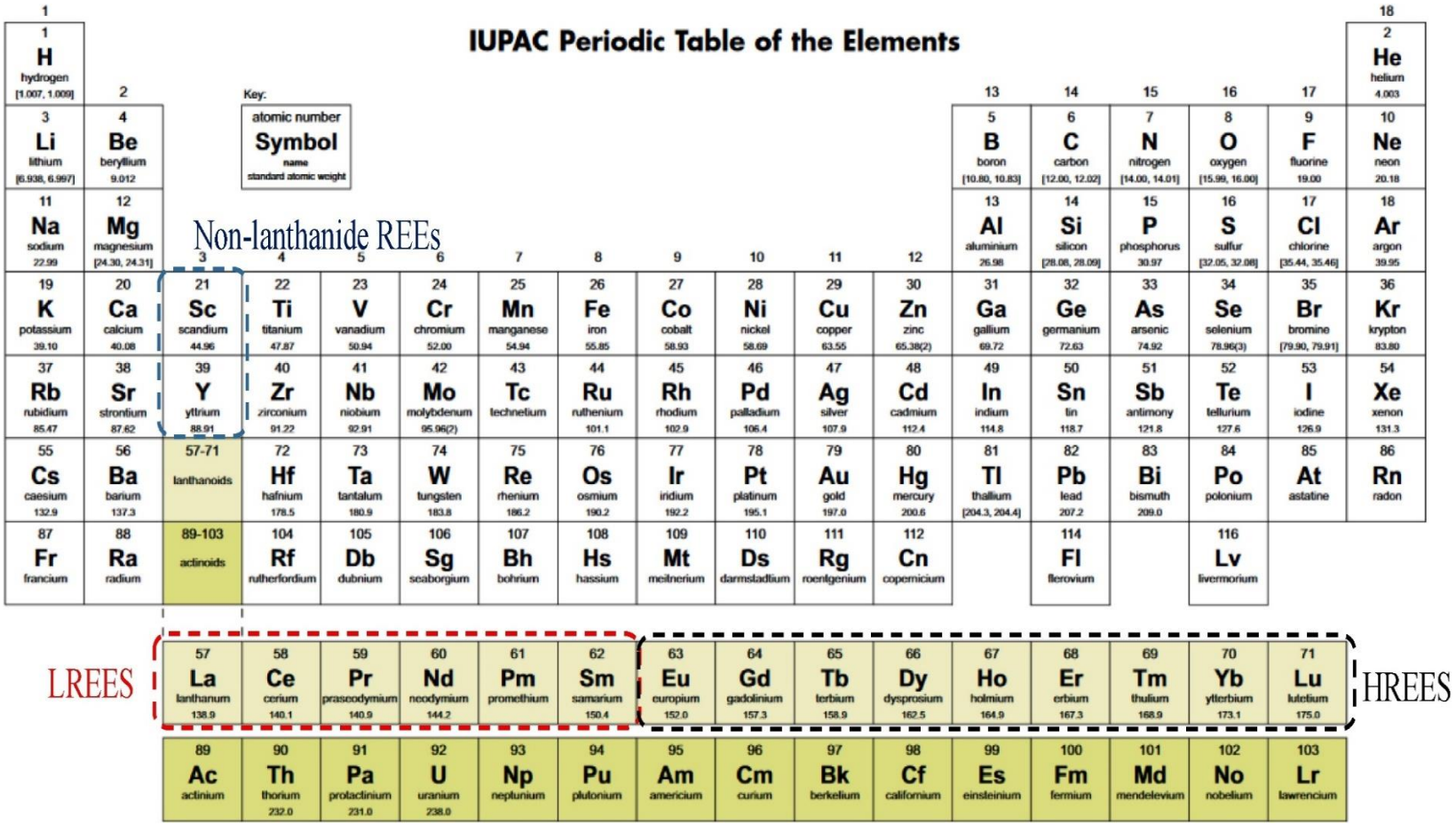

Figure 2.1 IUPAC Periodic table of the elements (Adopted from reference (Turpeinen et al., 2019) with permission from the Elsevier: see Figure F.1 in Appendix F)

Table 2.1 Atomic numbers of rare earth elements

No	Element	Symbol	Atomic Number (Z)
1	Lanthanum	La	57 (Aide & Aide, 2012)
2	Cerium	Ce	58 (Aide & Aide, 2012)
3	Praseodymium	Pr	59 (Aide & Aide, 2012)
4	Neodymium	Nd	60 (Aide & Aide, 2012)
5	Promethium	Pm	61 (Aide & Aide, 2012)
6	Samarium	Sm	62 (Aide & Aide, 2012)
7	Europium	Eu	63 (Aide & Aide, 2012)
8	Gadolinium	Gd	64 (Aide & Aide, 2012)
9	Terbium	Tb	65 (Aide & Aide, 2012)
10	Dysprosium	Dy	66 (Aide & Aide, 2012)
11	Holmium	Ho	67 (Aide & Aide, 2012)
12	Erbium	Er	68 (Aide & Aide, 2012)
13	Thulium	Tm	69 (Aide & Aide, 2012)
14	Ytterbium	Yb	70 (Aide & Aide, 2012)
15	Lutetium	Lu	71 (Aide & Aide, 2012)
16	Yttrium	Y	39 (Aide & Aide, 2012)
17	Scandium	Sc	21 (Aide & Aide, 2012)

2.2 Chemical Properties of REEs

The elements in REEs are usually found in the trivalent form. Nevertheless, cerium and europium can be found in bivalent, trivalent, and quadrivalent forms (Henderson, 1984). REEs ionic radius decreasing trend is found with increases in atomic number (Aide & Aide, 2012). The REEs with three-plus (+3) species are due to three electrons that can be removed from their last orbits (Greenwood & Earnshaw, 1984). The electron configuration in the f orbital starts in the lanthanides with cerium (Ce); that being said, there are no electrons in the f orbital of lanthanum (La) (Voncken, 2016). As mentioned above, the lanthanides (La to Lu), yttrium (Y), and scandium (Sc) are called REEs. Yttrium and scandium consist of lower atomic numbers, but lanthanides, yttrium,

and scandium exhibit similar chemical properties. The element with the smallest ionic radius in REEs is scandium, which shows different properties than the lanthanides (Henderson, 1984). The ionic radius of trivalent REEs is given in Table 2.2.

Table 2.2 Chemical properties and ionic radius of rare earth elements

No	Element	Electronic Configuration		Ionic radius (nm)	
1	La	[Xe] $5d^1 6s^2$	(Henderson, 1984)	0.1045	(Pereira et al., 2019)
2	Ce	[Xe] $4f^1 5d^1 6s^2$	(Henderson, 1984)	0.1010	(Pereira et al., 2019)
3	Pr	[Xe] $4f^3 6s^2$	(Henderson, 1984)	0.0997	(Pereira et al., 2019)
4	Nd	[Xe] $4f^4 6s^2$	(Henderson, 1984)	0.0983	(Pereira et al., 2019)
5	Pm	[Xe] $4f^5 6s^2$	(Henderson, 1984)	0.0970	(Pereira et al., 2019)
6	Sm	[Xe] $4f^6 6s^2$	(Henderson, 1984)	0.0958	(Pereira et al., 2019)
7	Eu	[Xe] $4f^7 6s^2$	(Henderson, 1984)	0.0947	(Pereira et al., 2019)
8	Gd	[Xe] $4f^8 6s^2$	(Henderson, 1984)	0.0938	(Pereira et al., 2019)
9	Tb	[Xe] $4f^9 6s^2$	(Henderson, 1984)	0.0923	(Pereira et al., 2019)
10	Dy	[Xe] $4f^{10} 6s^2$	(Henderson, 1984)	0.0912	(Pereira et al., 2019)
11	Ho	[Xe] $4f^{11} 6s^2$	(Henderson, 1984)	0.0901	(Pereira et al., 2019)
12	Er	[Xe] $4f^{12} 6s^2$	(Henderson, 1984)	0.0890	(Pereira et al., 2019)
13	Tm	[Xe] $4f^{13} 6s^2$	(Henderson, 1984)	0.088	(Pereira et al., 2019)
14	Yb	[Xe] $4f^{14} 6s^2$	(Henderson, 1984)	0.0868	(Pereira et al., 2019)
15	Lu	[Xe] $4f^{14} 5d^1 6s^2$	(Henderson, 1984)	0.0861	(Pereira et al., 2019)
	Xe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6 4d^{10} 3p^6 5s^2 5p^6$			
16	Y	[Kr] $4p^6 4d^1 5s^2$	(Aide & Aide, 2012)	0.0900	(Pereira et al., 2019)
17	Sc	[Kr] $4d^1$	(Aide & Aide, 2012)		
	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$			

2.3 Technological Applications of REEs

Some REEs are widely used as permanent magnets: terbium, neodymium, dysprosium, praseodymium, and samarium (Alonso et al., 2012)(Nansai et al., 2014). Yttrium, terbium, and

europium are used in light-emitting diodes (LED) (Seredin, Dai, Sun, & Chekryzhov, 2013). Permanent magnets that contain neodymium have been used in electric vehicles, computer hard drives, hybrid vehicles, and wind turbines (Eggert et al., 2016)(Meshram, Pandey, & Mankhand, 2015)(Gasser & Aly, 2013). Cerium oxide and lanthanum oxide are used in the fluid catalytic cracking catalysts in petroleum refining (Ye, Jing, Wang, & Fei, 2017). Steam reforming reactions are carried out by using a catalyst, which consists of lanthanum oxide and cerium oxides (Kourtelesis, Panagiotopoulou, Ladas, & Verykios, 2015)(Liguras, Kondarides, & Verykios, 2003). Fluorescent lamps contain a small proportion of cerium and lanthanum (Yang, Kubota, Baba, Kamiya, & Goto, 2013). Gadolinium is used in nuclear plants and the health care industry (Gupta & Krishnamurthy, 1992).

2.4 Solvent Extraction of REEs

Ion exchange and solvent extraction are two types of separation techniques that have been used to gain high purity single rare earth solutions. The first industrial-scale process was ion exchange process. However, nowadays ion exchange is only applied to obtain small scale REEs (Manjeet Kumar, 1994)(B. R. Reddy, Kumar, & Radhika, 2009). Solvent extraction is one of the vital chemical processes in which solutes are divided into two immiscible phases (B. R. Reddy et al., 2009). However, reagents are required to exchange ions across the interphase in ion exchange process. The most suitable technology for sorting out rare earth elements is solvent extraction (F. Peppard, Mason, & Maier, 1957)(D. F. Peppard, Mason, & Andrejasich, 1966)(M. L. P. Reddy, Prasada Rao, & Damodaran, 1993).

REEs are separated into their components in the solvent extraction process (L. Wang et al., 2010). The first step of solvent extraction, the REE is moved from the leachate to the organic phase. Then the REE forms a complex with the extractant. During this process, some portion of the REE remains in the aqueous phase. The distribution of REE between the aqueous phase and organic phase depends on extractant concentration, extractant type, diluents, pH, and temperature. When a mixture of REEs are used in a solvent extraction plant, there are many stages (Vahidi, Navarro, & Zhao, 2016). The solvent extraction process can be adjusted according to the mineral (Wuhua, Pijia, & Yongjun, 2010).

A typical laboratory level REEs solvent extraction experiment is carried out with REEs minerals, coal fly ash (Peiravi et al., 2018), waste materials (Pradhan, Swain, Prusty, Sahu, & Mishra, 2020),

and commercially available REO (99%) (Ohto et al., 1995)(Yuan et al., 2018). The first step is the mineral leach with acids, such as HNO_3, HCl, and H_2SO_4 (So, Walawalkar, Nichol, & Azimi, 2016). The leachate's available REEs content is measured by inductively coupled plasma-optical emission spectrophotometer (ICP-OES) (So et al., 2016). In many research projects, the authors used commercially available extractants such as Cyanex 272 (Sui & Huanga, 2019), Cyanex 572 (Zhou et al., 2019), CA-12 (W. Li, Wang, Meng, Li, & Xiong, 2007), and P507 (J. Wang, Chen, Xu, Yin, & Zhang, 2016). In rare cases, the extractant has been synthesized in a laboratory (Yuan et al., 2018)(J. Wang et al., 2016). Then the extractant is diluted with solvents like kerosene, benzene, and heptane (Atanassova, Kurteva, Lubenov, & Billard, 2015). The diluted extractants and the leachate are mixed by shaking and leaving to separate into two phases (Z. Zhao et al., 2017). Finally, the REE content in the aqueous phase is measured by ICP-OES (F. Li, Wang, Su, & Sun, 2019).

2.4.1 The distribution coefficient

Solvent extraction means mass transfer between two phases. The distribution coefficient is important in solvent extraction, described as the ratio of concentration in each phase (Divakar, Manikandan, & Sivakumar, 2008). The distribution coefficient is defined as follows (Equation 2.01),

$$D = \frac{M_{Organic}}{M_{Aqueous}} \quad \text{(2.01)}$$

However, rare earth element ion concentration in the organic phase is measured by the difference between the metal ion concentration of the feed (C_{Feed}) and metal concentration of the aqueous phase ($C_{Aqueous}$) after extraction. Many experiments were carried out as phase ratio 1:1 (Rout & Binnemans, 2014).

$$D = \frac{(C_{Feed} - C_{Aqueous}) \times V_{Aqueous}}{C_{Aqueous} \times V_{Organic}} \quad \text{(2.02)}$$

$$PR = \frac{V_{Aqueous}}{V_{Organic}} \quad \text{(2.03)}$$

$$D = \frac{(C_{Feed} - C_{Aqueous}) \times PR}{C_{Aqueous}} \quad \text{(2.04)}$$

2.4.2 Extraction efficiency

Similar to the distribution coefficient there is another parameter called extraction efficiency which also expresses the overall mass transfer from one phase to another; for example, the extraction efficiency is defined as follows (Equation 2.05 and 2.07) (Q. Zhao et al., 2019).

$$E = \left(\frac{M_{Organic}}{M_{Aqueous}+M_{Organic}}\right) \times 100 \quad \text{..... (2.05)}$$

$$E = \left(\frac{(C_{Feed}-C_{Aqueous})\times V_{Aqueous}}{C_{Aqueous}\times V_{Organic}+(C_{Feed}-C_{Aqueous})\times V_{Aqueous}}\right) \times 100 \quad \text{..... (2.06)}$$

$$E = \left(\frac{(C_{Feed}-C_{Aqueous})}{C_{Aqueous}\times PR+(C_{Feed}-C_{Aqueous})}\right) \times 100 \quad \text{..... (2.07)}$$

The distribution coefficient can be used to determine extraction efficiency (Equation 2.09) (Aly, Masry, Gasser, Khalifa, & Daoud, 2016).

$$E = \left(\frac{D}{D+\frac{V_{Aqueous}}{V_{Organic}}}\right) \times 100 \quad \text{..... (2.08)}$$

$$E = \left(\frac{D}{D+PR}\right) \times 100 \quad \text{..... (2.09)}$$

2.4.3 The separation factor

The separation factor is equal to the distribution coefficients of the REE_1 over the distribution coefficients of the REE_2. The selectivity between two REEs in any solvent extraction process is represented by the separation factor (Equation 2.10) (Gergoric, Ekberg, Steenari, & Retegan, 2017).

$$\alpha(REE_1, REE_2) = \frac{D_{REE_1}}{D_{REE_2}} \quad \text{..... (2.10)}$$

2.5 Solvent Extractants

Extractant is an essential chemical in any solvent extraction process that may contain a single substance or a mixture of substances. Solvent extractants are classified as acidic, chelating, solvation, and basic extractants (Parhi, Park, Nam, & Park, 2015)(Swain & Mishra, 2019).

2.6 Acidic Extractants

Under this designation, there are two types of extractants, namely carboxylic acid and phosphorous acid (Table 2.4). The reaction between the rare earth element (Ln) and organic anion (H_2R_2) can be expressed as follows (Equation 2.11) (D. F. Peppard et al., 1958),

$$Ln^{+n/}_{(aq)} + mH_2R_{2(Org)} \rightarrow MR_{n/}\frac{(m-n/)}{2}HR_{(Org)} + n/H^{+}_{(aq)} \quad \text{(2.11)}$$

The reaction between the REE and organic anion is produced complexes with organic anion (Mason, Bilobran, & Peppard, 1978)(S. Wu et al., 2018).

Table 2.3-Part 1 A few commercial acidic extractants for rare earth element extraction

Solvent Name	**Components**	**Commercial name**	**Reference**
Phosphorous acids	$C_{16}H_{35}O_4P$	D2EHPA	(Kuang, Zhang, Li, Wei, & Liao, 2017) (Q. Zhao et al., 2019)
	$C_{16}H_{35}PO_3$	EHEHPA	(Hailong, Yu, Yue, & Yundong, 2015)(J. Wang, Liu, Fu, Xie, & Huang, 2018)
	$C_{16}H_{35}O_2P$	Cyanex 272	(Bardestani, Kavand, & Askaripour, 2019) (Q. Zhao et al., 2019)
	$C_{16}H_{35}OPS$	Cyanex 302	(D. Wu, Xiong, Li, & Meng, 2005) (Q. Zhao et al., 2019)
		Cyanex 301	(Banda, Seok, & Seung, 2012)
	$C_{17}H_{38}NO_3P$	HEHAMP	(Q. Zhao, Zhang, Li, & Liao, 2018) (Q. Zhao et al., 2019)

Table 2.3-Part 2 A few commercial acidic extractants for rare earth element extraction

Solvent Name	**Components**	**Commercial name**	**Reference**
Phosphorous acids	$C_{17}H_{38}NO_3P$	HEHEHP	(Q. Zhao et al., 2019)
		HEHAPP	(Kuang et al., 2018)
		HDEHP	(Gruber & Carsky, 2020)
	$C_{16}H_{35}PO_4$	P204	(Gruber & Carsky, 2020)
	$C_{16}H_{35}PO_2$	P227	(J. Wang, Xie, Liu, & Wang, 2018)
	$C_{12}H_{27}PO_2$	HYY-2	(J. Wang et al., 2016)
Carboxylic acids		Naphthenic acids	(Liao et al., 2001)
		Versatic acids	(Zheng, Gray, & Stevens, 1991)
		TODGA	(Turanov, Karandashev, & Khvostikov, 2017)

2.6.1 Phosphorous acid extractants

Several types of organophosphorus, such as mono-2-ethylhexyl, di-2,4,4-trimethylpentyl-dithiophosphinic acid, di (2-ethylhexyl) phosphoric acid, di-2,4,4-trimethylpentyl-monothiophosphinic acid, and, 2-ethylhexyl phosphonic acid are used for REEs extraction (Kuang et al., 2017)(Hailong et al., 2015)(Bardestani et al., 2019). The distribution coefficients of REE ions are correlated with HCl concentration with mono-2-ethylhexyl in toluene and chloride (F.

Peppard et al., 1957). The hydrophilic behavior of D2EHPA causes more reactions close to the aqueous phase (Thakur, 2017). Ferraro et al. found that when heavy metals were reacting at lower pH values, gels can be formed in the aqueous phase (Ferraro, Cristallini, & Fox, 1967). Organometallic complexes can be found in the organic phase when EHEHPA, D2EHPA, and Cyanex 272 react with REEs (Torkaman, Safdari, Torab-mostaedi, & Moosavian, 2014). The position of yttrium for phosphorous acids such as HEHAPP (Kuang et al., 2018), and HEEHP is in between holmium and erbium (Q. Zhao et al., 2018). However, the yttrium position is in between dysprosium and holmium for extractants such as Cyanex 272, TOPO, and Cyanex 572 as was found by Radhika et al. (Radhika, Kumar, Kantam, & Reddy, 2010). The solvent extraction order of D2EHPA starts from the highest atomic number and moves to the lowest one in the lanthanides series (Ohto et al., 2018)(Pierce & Peck, 1963).

2.6.2 Carboxylic acid extractants

Carboxylic acids are inexpensive compared to other available solvent extractants. The available carboxylic acids are naphthenic acids and versatic acids. The extraction pattern of carboxylic acids increases with the atomic number of lanthanides. However, it was found that the position of yttrium for naphthenic acid is in between gadolinium and holmium, and for versatic acid 10 is in between cerium and neodymium (Zheng et al., 1991). The acidity of the carboxylic acid and structure of the acidic extractant causes yttrium's unusual behavior (du Preez & Preston, 1992). Naphthenic acids consist of high solubility in the aqueous phase. Therefore, one can find naphthenic acid composition deviations when it is applied to water. Hence, two carboxylic acids were developed as an alternative regent: sec-nonyl phenoxy, and sec-octyl phenoxy acetic acid. (L. Deqian, Zhonghuai, Wenzhong, Shulan, & Gengxiang, 1994). Wang et al. found that sec-nonyl phenoxy acetic acid was better than versatic 10 for some REEs (Y. G. Wang, Yue, Li, Jin, & Li, 2002).

2.7 Chelating Extractants

The chelating extractants follow the cation ion-exchange mechanism. However, after the chelating extractant reacts with the metal, the produced organic complexes are maintained by the organic anion (Hudson, 1982). Urbanski et al. examined the extraction of Eu from nitrate solutions with chelating extractants and concluded that the extraction performance of chelating extractants was lower than acidic extractants (Urbanski, Fornari, & Abbruzzese, 1996).

2.8 Solvation Extractants

Solvation extractants such as dibutyl-butyl phosphonate, tri-n-butyl-phosphate, and tri-n-octyl phosphine oxide have been used for rare earth separations. The extraction ability of the REEs with TBP increases with increasing atomic number. However, REEs heavier than Sm cannot be separated in the nitric system. The solvation extractants are tabulated in Table 2.4. The overall reaction is as follows (Equation 2.12) (F. Peppard et al., 1957),

$$Ln^{3+} + 3NO_3^- + 3TBP \rightarrow Ln(NO_3)_3.(TBP)_3 \quad (2.12)$$

Table 2.4 A few commercial solvation extractants for rare earth element extraction

Solvent Name	**Components**	**Commercial name**	**Reference**
Phosphorous ester		TBP	(Y. Liu, Seok, & Seung, 2015)
Phosphine oxides		TOPO, Cyanex 921	(Panda, Devi, & Mishra, 2012)
	$C_{18}H_{39}$ OP	Cyanex 923	(Thuy, Nguyen, & Lee, 2019)
	$C_{20}H_{43}$ OP		
	$C_{22}H_{47}$ OP		
	$C_{24}H_{51}$ OP		

2.9 Basic Extractants

The mechanism of basic extractants is that they produce anionic complexes with metal ions. The basic extractants are only active in the availability of potent anionic ligands. Yamani and Sabana found that sulfate media was better than chloride media for REEs separation (El-Yamani & Shabana, 1985). Tri-octyl methyl ammonium (Quaternary ammonium salts) nitrate can be used for separating REEs (Desouky, Daher, Abdel-Monem, & Galhoum, 2009). Tri-octyl

methylammonium reagents are strong base extractants. Moreover, they need a low number of salting-out reagents compared to amines. The extraction efficiency of LREEs (La, Ce, Pr, Nd, Pm, Sm) by Tricapryl methyl ammonium in nitrate media higher than HREEs (Tm, Er, Eu, Tb, Lu, Dy, Gd, Ho, Yb). However, these findings go against the behavior of acidic extractants and solvating extractants. All experimental results showed that the extraction efficiency of REEs increases with the lowest atomic number to the highest atomic number for acidic extractants and solvating extractants. Therefore, it was revealed that Tri-octyl methyl ammonium reagents could be used for removing LREEs from a solution (Černá, Volaufová, & Rod, 1992).

Xenotime consists of 60% yttrium oxide. Yttrium performs as an LREEs with thiocyanate media. However, media yttrium behaves like HREEs in the presence of nitrate. Hence, the yttrium extraction process is as follows: first Xenotime is leached with nitrate media then LREEs can be separated using thiocyanate media (D. Lu, Horng, & Hoh, 1989). The available basic extractants are given below in Table 2.5.

Table 2.5 A few commercial basic extractant for rare earth element extraction

Solvent Name	**Components**	**Commercial name**	**Reference**
Primary amines		Primene JMT	(Desouky et al., 2009)
Tertiary amines	$C_{24}H_{51}N$	TEHA	(Thuy et al., 2019)
Quaternary amines		Alimine 336	(Y. Liu et al., 2015)
		Aliquat 336	(Padhan & Sarangi, 2017)
		Alimine 308	(Banda, Jeon, & Lee, 2012)

2.10 Effective Parameters for The Distribution Coefficient

Solvent extraction process for separation of REEs is a complex process, and the distribution coefficient depends on many parameters such as pH, extraction concentration, extractant type, equilibration time, temperature, diluents concentration, and diluent type (Yeong et al., 2016)(Desouky et al., 2009). Many researchers experimentally studied the effect of one or more than one parameter and discussed equations related to them (Q. Zhao et al., 2018).

2.11 Effect of Diluents

The solvent phase (organic phase) consists of active extractant and inert diluent (Desouky et al., 2009). Wu et al. found a problem in the phase separation step because kerosene reduced the concentration of the extractant (S. Wu et al., 2017). The lowest extraction percentage was observed in the absence of hexanol. Furthermore, with an increase in the proportion of hexanol, extraction efficiency decreases to 50:50. Desouky et al. experimentally evaluated the extraction of Y(III) by Primene-JMT with six different diluents. They observed the highest yttrium extraction with kerosene (Desouky et al., 2009).

2.12 Effect of Equilibration Time (log D vs. t)

The duration of equilibration time can be divided into two parts. First is the time required to establish equilibrium, and phase contact duration. Knyaz'kina et al. carried out experiments to evaluate the effect of equilibration time for the extraction of Mo(VI) using Cyanex 272 (Knyaz'kina et al., 2010). Kumari et al. experimentally found that more than 80% Neodymium extracted using EHEHPA with 5-minute equilibration time. According to their findings, extraction efficiency increased until the 5^{th}-minute and then kept constant (Kumari, Panda, Young, Thriveni, & Kumar, 2019). Although Radhika et al. observed the best equilibration time as 5 minutes, they carried out all experiments until 15 minutes (Radhika et al., 2010). Figure 2.2 shows that extraction efficiency increases until the 6^{th}-minute and then slightly reduces until the 15^{th}-minute (Desouky et al., 2009).

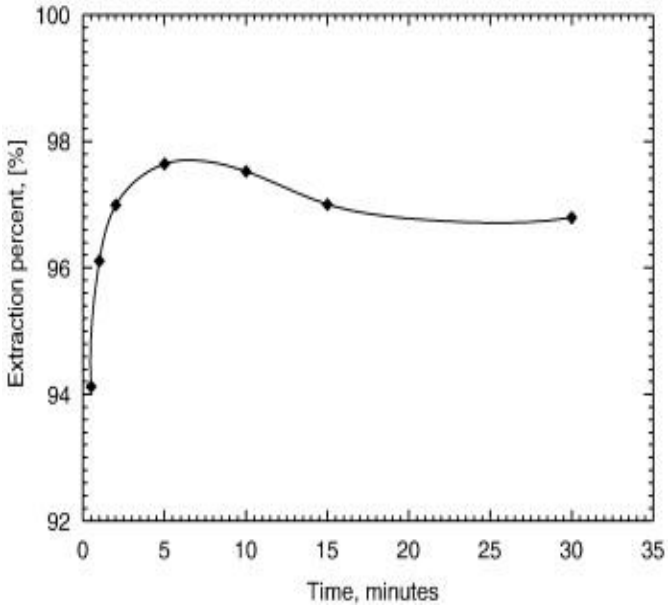

Figure 2.2 Effect of equilibrium time on yttrium extraction efficiency (Adopted from reference (Desouky et al., 2009) with permission from the Elsevier: see Figure F.2 in Appendix F)

2.13 Effect of Temperature (log D vs 1/T)

The extraction process of REEs into the organic phase from the aqueous phase comprises considerable alterations in both enthalpy and entropy, which would lead to significant temperature changes. Desouky et al. found that the extraction efficacy of yttrium was decreased from 97.8% to 88.9% by increasing the temperature from 25 ºC to 60 ºC (Desouky et al., 2009). Figure 2.3 shows log D vs. 1000/T plot adopted from the Desouky et al research paper. The graph represents the extraction of yttrium(III) by Primene-JMT (Desouky et al., 2009). According to Figure 2.3, the relationship between log D and T is mentioned in Equation 2.13. Nevertheless, Lu and Liao mentioned the gradient in log D vs 1000/T as Equation 2.14 (Y. Lu & Liao, 2016). There is a significant difference between Desouky et al. log D vs. 1000/T plot and Lu and Lia log D vs. 1000/T plot, which is Desouky et al.'s positive gradient and Lu and Lia's negative gradient.

$$\log D = \mathrm{GRD}_T\left(\frac{1}{T}\right) + \mathrm{C}_T \quad (2.13)$$

$$\frac{d(\log D)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H}{2.303 \times R} \quad (2.14)$$

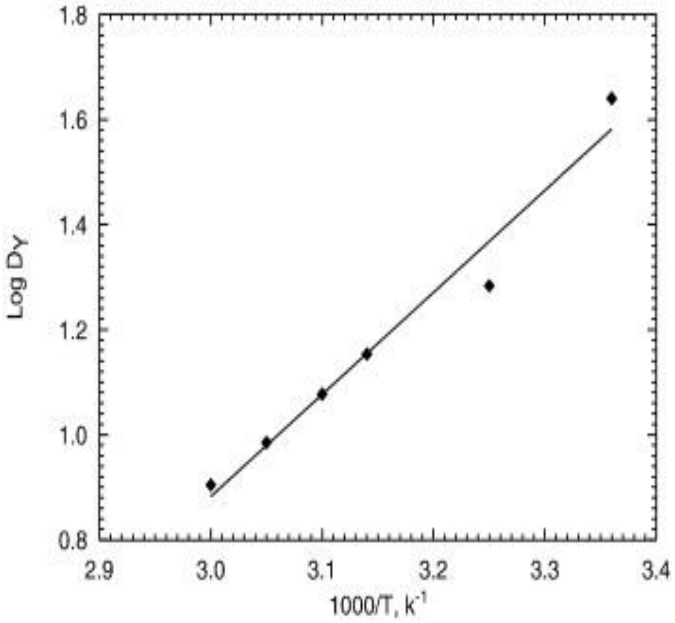

Figure 2.3 Effect of temperature on the distribution coefficient for yttrium (Adopted from reference (Desouky et al., 2009) with permission from the Elsevier: see Figure F.3 in Appendix F)

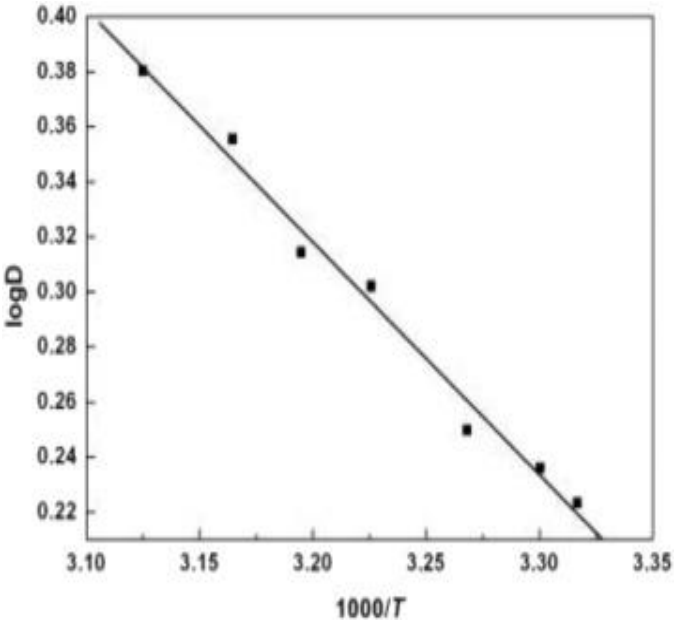

Figure 2.4 Effect of temperature on the distribution coefficient for ytterbium (Adopted from reference (Y. Lu & Liao, 2016) with permission from the Elsevier: see Figure F.4 in Appendix F)

2.14 Effect of Extractant Concentration (log D vs log(H_2R_2))

Kina et al. carried out many experiments to analyze the effects of extractant concentration on extraction efficiency (Knyaz'kina et al., 2010). It was observed that extraction efficiency increases with concentration up to 0.1346 M and then maintains a constant value. Nevertheless, it was found that log D value increases nonlinearly with concentration. Solvent extraction of Pr, Eu, Tb, Ho, and Yb were carried by Inba et al., who presented their results in log D vs log (H_2R_2) plot (Inaba et al., 1993). It is interesting to note that this graph is not a straight line for Eu and Yb for $(HR)_2=10^{-2}$-10^{-4} M. In a smaller $(HR)_2$ concentration, some REEs are formed as $Ln(R)_3.2(HR)$. Extraction of Nd(III) with HNO_3 using Cyanex 272 was conducted by Panda et al. (Panda, Devi, & Mishra, 2013). Moreover, Quinn et al. found two slops for two EHEHPA concentration ranges (Quinn et al., 2015). Torkman et al carried out an experiment set with D2EHEPA as the extractant and samarium as the REE. The significant finding was that the distribution coefficient increased with extractant concertation until 0.12 M. After that, the distribution coefficient started to decline (Torkaman, Safdari, Torab-mostaedi, Moosavian, & Asadollahzadeh, 2015). Equation 2.15 represents the log D vs. log(H_2R_2) as mentioned in Figure 2.5.

$$\log D = \mathrm{GRD}_{H_2R_2}(\log (H_2R_2) + \mathrm{C}_{H_2R_2} \quad \text{(2.15)}$$

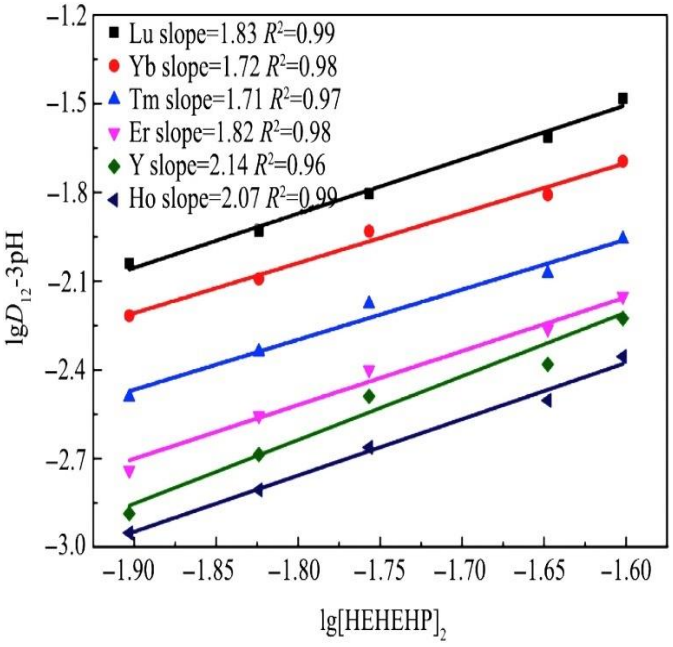

Figure 2.5 Effect of extractant concentration on the distribution coefficient (Adopted from reference (Q. Zhao et al., 2019) with permission from the Elsevier: see Figure F.5 in Appendix F)

2.15 Effect of Aqueous to Organic Phase Ratio (log D vs PR)

The aqueous to organic phase ratio can significantly influence extraction efficacy. Desouky et al. reported that the highest extraction efficiency was observed at the 1:1 ratio (Desouky et al., 2009). Wu et al. experimentally proved that REEs' distribution coefficient is directly proportional to phase ratio (S. Wu et al., 2017). Kumari et al. mentioned that REEs extraction efficiency depends on the organic phase volume (Kumari et al., 2019). Rho et al. found that the incremental increase of phase ratio from 0.2 to 5 resulted in the improvement of neodymium extraction by 17% (Rho, Sun, & Cho, 2019).

2.16 Effect of pH (log D vs pH)

The effect of pH on the distribution coefficient is necessary to determine REEs in divalent or trivalent form. The highest extraction efficiency of 97.8% was observed at an equilibrium pH value of 1.56. After the point where the highest extraction efficiency occurred, yttrium extraction efficiency decreased gradually (Desouky et al., 2009). Kumari et al. carried out extraction experiments using D2EHPA as extractant. As the authors mentioned in their paper, the extraction efficiency of REEs increased until the pH value of 2.0 after that extraction efficiency remained at a nearly constant value (Kumari et al., 2019). The relationship log D vs. pH, is indicated in Equation 2.16. The lanthanides relationship with its atomic number is shown in Figure 2.6 (Singh et al., 2006).

$$\log D = \mathrm{GRD}_{pH}(\mathrm{pH}) + \mathrm{C}_{pH} \quad (2.16)$$

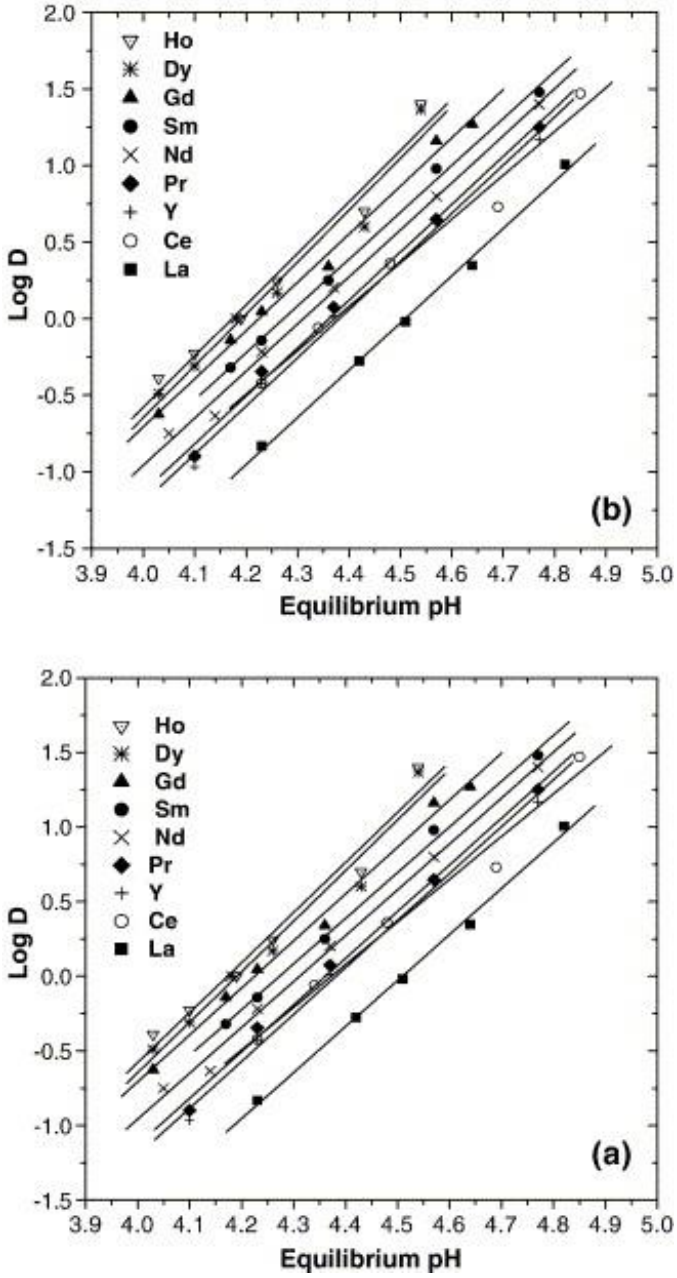

Figure 2.6 Effect of pH on the distribution coefficient (Adopted from reference (Singh et al., 2006) with permission from the Elsevier: see Figure F.6 in Appendix F)

CHAPTER 3

MATERIALS AND METHOD

3.1 Materials

The essential data is taken from the literature to predict the distribution coefficient of the solvent extraction of REEs. The experimental datasets were chosen with at least three REEs present in each set. More than seven hundred data points comprising of a logarithmic value of the distribution coefficient datapoints were analyzed in this project (Table 3.1). The core objective of this work is to introduce an advanced model that can be used to calculate the distribution coefficient of REEs. In this regard, various types of solvent extractants were considered, such as Cyanex 272, Cyanex 572, D2EHEPA, EHEHPA, EHEPA, TBDGA, DNPP, HEHAMP, HEHEMP, HL4, HEHAPP, Cekatonic, Neo heptanol, Cyanex 301, Cyanex 923, HEDHP, HEH/EHP, and P227. The experimental database for log D vs pH is shown in Table 3.1. The proposed model validity for log D vs log (H_2R_2) was checked by using Table 3.2 data.

Table 3.1-Part 1 Experimental data base for log D vs. pH plot

No	Solvent Extractant	Concentration M	No of Elements	No of Data Points	Reference	Description	MAE
1	Cyanex 272	1	11	53	(Quinn et al., 2015)	Table 3.6	0.23
2	Cyanex 572	1	4	23	(Quinn et al., 2015)	Table A.1	0.26
3	D2EHEPA	1.56	8	40	(Ohto et al., 1995)	Table A.2	0.35
4	EHEHPA	1.61	8	40	(Ohto et al., 1995)	Table A.3	0.20
5	EHEPA	1	4	22	(Quinn et al., 2015)	Table A.4	0.09
6	Cyanex 272	0.1	5	23	(Komatsu & Freiser, 1989)	Table A.5	0.56
7	Cyanex 272 (0.1 M) with TOPO (0.01 M)	0.1	5	22	(Komatsu & Freiser, 1989)	Table A.6	0.32
8	Cyanex 272	0.1	5	24	(Komatsu & Freiser, 1989)	Table A.7	0.47
9	TBDGA	0.25	4	32	(D. F. Peppard et al., 1958)	Table A.8	0.24
10	Cyanex 272	0.1	13	70	(L. I. Deqian, 2017)	Table A.9	0.33
11	D2EHEPA	N/A	4	20	(Chen et al., 2020)	Table A.10	0.38
12	DNPP	0.2	3	14	(Anitha et al., 2014)	Table A.11	0.47

Table 3.1-Part 2 Experimental data base for log D vs. pH plot

No	Solvent Extractant	Concentration M	No of Elements	No of Data Points	Reference	Description	MAE
13	Cyanex 572	N/A	5	35	(Y. Wang et al., 2015)	Table A.12	0.62
14	HEHAMP+HEHEMP	0.1	6	54	(Q. Zhao et al., 2019)	Table A.13	0.09
15	HL4	0.002	6	30	(Y. Lu & Liao, 2016)	Table A.14	0.36
16	HEHAPP	0.05	4	24	(Kuang et al., 2018)	Table A.15	0.76
17	Cekaonic Acid	0.56	9	45	(Singh et al., 2006)	Table A.16	1.09
18	Neo heptanol	0.73	8	40	(Singh et al., 2006)	Table A.17	1.49
19	Cyanex 301(0.2 M) +Cyanex 923(0.01 M)		8	48	(M. L. P. Reddy et al., 1999)	Table A.18	0.28
20	HEDHP (0.04M) + HEH/EHP (0.06M)		4	36	(Zhang et al., 2008)	Table A.19	0.37
21	EHEHPA	N/A	8	48	(Registered et al., 2007)	Table A.20	0.27
22	P227	0.16	6	33	(Chen et al., 2020)	Table A.21	0.07
			138	776			

Table 3.2 Experimental data base for log D vs. log(H_2R_2) plot

No	Solvent Extractant	pH	No of Elements	No of Data Points	Reference	Description	MAE
1	EHEHPA	N/A	8	48	(Registered et al., 2007)	Table 3.7	0.21
2	HEDHP	1.3	3	15	(Zhang et al., 2008)	Table D.1	0.11
3	HEH/EHP	1.9	3	15	(Zhang et al., 2008)	Table D.2	0.08
4	HEHEHP	N/A	6	30	(Q. Zhao et al., 2019)	Table D.3	0.61
5	Cyanex 272	N/A	4	20	(Inaba et al., 1993)	Table D.4	0.27
6	D2EHEPA	N/A	3	18	(S. Wu et al., 2017)	Table D.5	0.35
	Total		27	146	5		

3.2 Factors Affecting Data Collection

The parameters affecting the distribution coefficient include extractant concentration, temperature, pH, phase ratio, and equilibration time. As stated in the literature review, the most influential parameters among these factors are extractant concentration, temperature, and pH.

Table 3.3 Factors affecting the data collection

No	Type	Data Points
1	Extractants	18
2	Concentrations	11
3	Temperature	1
4	Phase Ratio	1
5	Equilibration time	2
6	Diluents	2

3.3 Performance Evaluation

The best-fitting curve is determined using the regression equation (Equation 3.04). Here, 'U' represents the fluctuations of estimated log D values and the mean of experimental log D values. Then 'Q' gives fluctuations between experimental log D values and estimated log D values (Xuanxuan, 2018).

$$\log D_k^{est} = mx_k + c \quad (3.01)$$

$$Q = \sum_{k=1}^{n} \left(\log D_k^{exp} - \log D_k^{est}\right)^2 \quad (3.02)$$

$$U = \sum_{k=1}^{n} \left(\log D_k^{est} - \overline{\log D^{exp}}\right)^2 \quad (3.03)$$

$$R^2 = 1 - \frac{Q}{U} = 1 - \frac{\sum_{k=1}^{n} \left(\log D_k^{exp} - \log D_k^{est}\right)^2}{\sum_{k=1}^{n} \left(\log D_k^{est} - \overline{\log D^{exp}}\right)^2} \quad (3.04)$$

The mean of the absolute difference between the experimental values and estimated values is represented by the Mean Absolute Error (Equation 3.05) (S. Liu & Papanikolaou, 2020).

$$MAE = \frac{1}{n}\sum_{k=1}^{n}\left|\log D_k^{exp} - \log D_k^{est}\right| \quad (3.05)$$

The standard deviation is evaluated as follows (Equation 3.07) (S. Liu & Papanikolaou, 2020).

$$\mu = \frac{1}{n}\sum_{k=1}^{n} x_i \quad (3.06)$$

$$\sigma^2 = \frac{1}{n}\sum_{k=1}^{n}(x_i - \mu)^2 \quad (3.07)$$

3.4 Methodology

The entire REE series can be found in the log D vs. pH plot, log D vs. log(H_2R_2) plot, and log D vs. 1/T plot (Registered et al., 2007)(Singh et al., 2006). Among these three plots, the gradient is one value for the REEs in log D vs. pH plot. Hence, the available experimental results from the literature for the REEs log D variations with pH were used to propose a model. After that, the proposed model's applicability in log D vs. log (H_2R_2) was checked. Finally, the separation factor, and extraction efficiency prediction using the proposed model was discussed.

3.5 Solvent Extraction Equilibrium

In this section, to analyze the distribution coefficient, most straightforward solvent extraction equilibrium equation was analyzed, as shown in Equation 3.08. The effect temperature has on the distribution coefficient calculations was introduced via thermodynamic theory. For instance, researchers have proposed a model in which temperature is inversely proportional to the distribution coefficient. As a case study, here consider acidic solvent extraction equilibrium equation. For more complicated system as acidic extractant in chloride media, solvation extractant in nitric media, basic extractant in chloride media, and basic extractant in nitrate media were described later.

3.5.1 Solvent extraction equilibrium equation

As mentioned in literature review, there are a variety of extractants. The solvent extraction of REEs with acidic extractant was reported as follows (Equations 3.08,3.09, and 3.10) (Torkaman, Moosavian, Torab-Mostaedi, & Safdari, 2013)(du Preez & Preston, 1992),

$$Ln_{(aq)}^{+n/} + \frac{m}{2}(HR)_{2(org)} \rightarrow Ln(R)_{n/}\left(m - n/\right)RH_{(org)} + n/H_{(aq)}^{+} \quad (3.08)$$

$$K_{ex} = \frac{\left[Ln(R)_{n/}(m-n/)RH\right][H^+]^{n/}}{\left[Ln^{+n/}\right][(HR)_2]^{\frac{m}{2}}} \quad (3.09)$$

$$\log K_{ex} = \log D - \frac{m}{2}\log(H_2R_2) - n/pH \quad (3.10)$$

3.5.2 Energy of solvent extraction equilibrium reaction

The Gibbs free energy, standard formation of enthalpy, and standard entropy of formation are used to measure equilibrium position (J. Wang et al., 2016)(Pereira et al., 2019). By using equations 3.11,3.12, and 3.13, we can obtain Equation 3.18.

$$\Delta G^o = \Delta H^o - T \times \Delta S^o \quad (3.11)$$

$$\Delta G^o = -R \times T \times lnK_{ex} \quad (3.12)$$

In Equation 3.12, *ln* K_{ex} implies the base e logarithm. However, the distribution coefficient was tabulated in plots with log form, which describes the base 10 logarithms. For an analytical purpose, Equations 3.12 was converted to Equation 3.14 by using Equation 3.13.

$$lnK_{ex} = 2.303logK_{ex} \quad (3.13)$$

$$\Delta G^o = -R \times T \times 2.303logK_{ex} \quad (3.14)$$

$$logK_{ex} = -\frac{\Delta G^o}{2.303\times R\times T} \quad (3.15)$$

$$logK_{ex} = -\frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.16)$$

Here, Equation 3.10 was the solvent extraction equilibrium constant for acidic extractant as the extractant. Equation 3.17 was the most important equation in this research, which was derived based on equilibrium energy. Subtracting Equation 3.10 and 3.16, we can obtain Equation 3.18. The trick was to subtract two equations so that the effect of temperature was added. The standard enthalpy of formation and standard entropy of formation are essential for this analysis.

$$\log D = \frac{m}{2}\log(H_2R_2) + n/pH - \frac{\Delta G^o}{2.303\times R\times T} \quad (3.17)$$

$$\log D = \frac{m}{2}\log(H_2R_2) + n/pH - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.18)$$

As shown in Equation 3.18, the equilibrium relationship was proven by Cheraghi et al. for the solvent extraction of vanadium (Cheraghi, Shaker, & Keshavarz, 2015). Three parameters are available in Equation 3.20 to evaluate the distribution coefficient. Three different plots can be obtained using Equation 3.18 (Equation 3.22, 3.26, and 3.30). We assume for now that each plot has only one variable, and all other parameters are constant values. For example, the only parameter changes in log D vs. pH plot was pH and all other parameters are constant values (extractant concentration, temperature, phase ratio, equilibration time, diluent type, and diluent concentration).

log D vs pH (Effect of pH)

$$\log D = n^{/} pH + \frac{m}{2}\log(H_2R_2) - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.19)$$

$$GRD_{pH} = n^{/} \quad (3.20)$$

$$C_{pH} = \frac{m}{2}\log(HR)_2 - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.21)$$

$$\log D = GRD_{pH} pH + C_{pH} \quad (3.22)$$

log D vs log (H_2R_2) (Effect of extractant concentration)

$$\log D = \frac{m}{2}\log(H_2R_2) + n^{/} pH - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.23)$$

$$GRD_{H_2R_2} = \frac{m}{2} \quad (3.24)$$

$$C_{H_2R_2} = n^{/} pH - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.25)$$

$$\log D = GRD_{H_2R_2}\log(H_2R_2) + C_{H_2R_2} \quad (3.26)$$

log D vs T (Effect of temperature)

$$\log D = -\frac{\Delta H^o}{2.303\times R\times T} + n^{/} pH + \frac{m}{2}\log(H_2R_2) + \frac{\Delta S^o}{2.303\times R} \quad (3.27)$$

$$GRD_T = -\frac{\Delta H^o}{2.303\times R} \quad (3.28)$$

$$C_T = n^{/} pH + \frac{m}{2}\log(H_2R_2) + \frac{\Delta S^o}{2.303\times R} \quad (3.29)$$

$$\log D = GRD_T \frac{1}{T} + C_T \quad \text{(3.30)}$$

Table 3.4 A brief description about the gradient and intercept for log D vs pH, log D vs log (H_2R_2) and log D vs 1/T plots

No	Correlation	Equation	Gradient	Intercept
1	$\log D \; vs \; pH$	$\log D = GRD_1 pH + C_1$	$GRD_{pH} = n/$	$C_{pH} = \frac{m}{2}\log(HR)_2 - \frac{\Delta H^o}{2.303 \times R \times T} + \frac{\Delta S^o}{2.303 \times R}$
2	$\log D \; vs \; \log(H_2R_2)$	$\log D = GRD_{H_2R_2}\log(HR)_2 + C_{H_2R_2}$	$GRD_{H_2R_2} = \frac{m}{2}$	$C_{H_2R_2} = n/pH - \frac{\Delta H^o}{2.303 \times R \times T} + \frac{\Delta S^o}{2.303 \times R}$
3	$\log D \; vs \; \frac{1}{T}$	$\log D = GRD_T \frac{1}{T} + C_T$	$GRD_T = -\frac{\Delta H^o}{2.303 \times R}$	$C_T = n/pH + \frac{m}{2}\log(HR)_2 + \frac{\Delta S^o}{2.303 \times R}$

3.6 Effect of pH (log D vs pH)

3.6.1 Comparison of two REEs in log D vs pH plot

Recall Equation 3.22, where the distribution coefficient evaluates with changing pH values. Many experiments were found the gradient of log D vs. pH plot as approximately 3 (Table 3.6). The formed complex in a solvent extraction equilibrium system was the same complex for all REEs for an extractant concentration value (Ohto et al., 1995). This implies that all REEs have one value for '$\frac{m}{2}\log\ (HR)_2$', in which all of the experiments are carried out. The intercept of the log D vs. pH equation was calculated by Equation 3.32.

$$GRD_{pH\ REE1} = GRD_{pH\ REE2} = n/ = 3 \quad \text{(3.31)}$$

$$C_{pH\ REE1} = \frac{m}{2}\log(HR)_2 - \frac{\Delta H^o_{REE\ 1}}{2.303 \times R \times T} + \frac{\Delta S^o_{REE\ 1}}{2.303 \times R} = \frac{m}{2}\log(HR)_2$$

$$+ \log K_{exREE\ 1} = \frac{m}{2}\log(HR)_2 - \frac{(\Delta G^o_{REE\ 1})}{2.303 \times R \times T} \quad \text{(3.32)}$$

$$C_{pH\ REE2} = \frac{m}{2}\log(HR)_2 - \frac{\Delta H^o_{REE\ 2}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 2}}{2.303\times R} = \frac{m}{2}\log(HR)_2$$

$$+ \log K_{ex\ REE\ 2} = \frac{m}{2}\log(HR)_2 - \frac{(\Delta G^o_{REE\ 2})}{2.303\times R\times T} \quad \text{(3.33)}$$

$$\Delta C_{pH\ REE} = C_{pH\ REE1} - C_{pH\ REE2} = -\frac{(\Delta H^o_{REE\ 1} - \Delta H^o_{REE\ 2})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\ 1} - \Delta S^o_{REE\ 2})}{2.303\times R} =$$

$$logK_{ex\ REE\ 1} - \log K_{ex\ REE\ 2} = -\frac{(\Delta G^o_{REE\ 1} - \Delta G^o_{REE\ 2})}{2.303\times R\times T} \quad \text{(3.34)}$$

To make calculations easier, Equations 3.34 can be modified as Equation 3.35.

$$\Delta C_{pH\ REE}{}' = C_{pH\ REE\ n} - C_{pH\ REE\ k} = -\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303\times R} = logK_{ex\ REE\ n} -$$

$$\log K_{ex\ REE\ k} = -\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303\times R\times T} \quad \text{(3.35)}$$

Where n>k, n and k values are tabulated in Table 3.6.

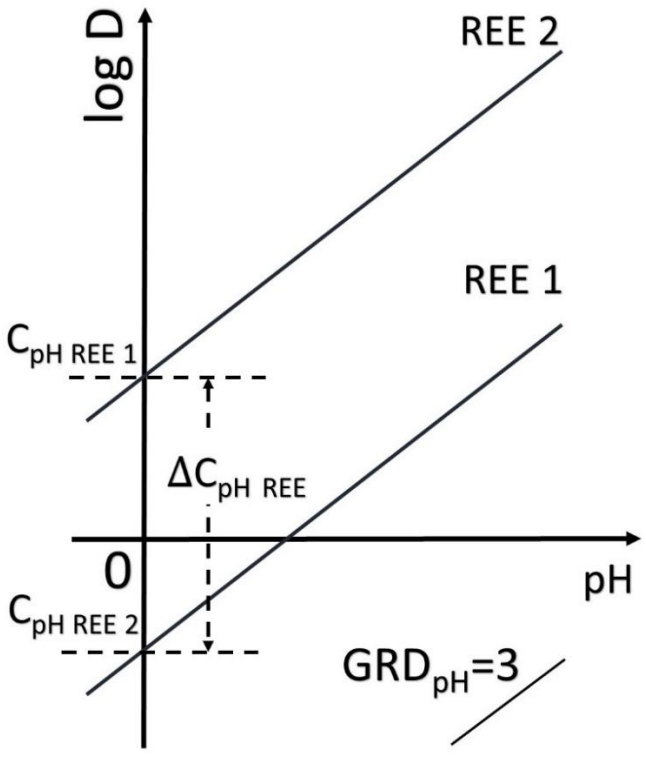

Figure 3.1 The comparison of two adjacent rare earth elements for log D vs pH plot

3.6.2 Model formulation

The results presented below show that there was a clear relationship between atomic number and log D vs. pH curves. For example, deviation between two adjacent lanthanides was approximately 0.3 (Table 3.6). The proposed model was introduced based on the fact that the gradient of the log D vs. pH curve must be a natural number (a positive integer). Nevertheless, most of solvent extractions of REEs gradients values have been found with a decimal number (Table 3.6). Hence, we need to find the best-fitting curve for the available experimental values (Table 3.6).

The intercept differences between two adjacent lanthanides are shown in Table 3.6. A statistical analysis was carried out to determine the mean value and standard deviation of the data set. Based on the mean value, a model was proposed to determine the entire REE series. According to the proposed model, the relationship between the lanthanide's intercepts in log D vs. pH plot and atomic number was linear.

$$C_n = 0.3484(n) + C \quad \text{(3.36)}$$

The above-mentioned model has been modified to determine the intercept of any REE as follows,

$$C_n - C_k = 0.3484(n - k) \quad \text{(3.37)}$$

Table 3.5 A brief description about the statistical analysis of the intercept difference of two adjacent rare earth elements

No	Description	Value
1	No of points	58
2	Maximum	0.8
3	Minimum	-2.3
4	Mean	-0.3484
5	Standard Deviation	0.47445

3.6.3 Determining of the yttrium position

It has been proven by experimental findings that the intercept value of yttrium falls in between holmium and erbium (Quinn et al., 2015). However, based on yttrium's atomic number (39), its

intercept value should be far away from the lanthanide (57-71). Moreover, the yttrium position based on the ionic radius is in between holmium and erbium. A clear linear relationship between the ionic radius of lanthanides and its atomic number was observed (Table 3.7 and Equation 3.38). This implies that there is a relationship between the ionic radius of REEs and intercept deviation of REEs in log D vs. pH plot. Hence, 'n' value in the model was redefined based on the ionic radius of REEs. The linear relationship of lanthanides between the ionic radius and atomic number is useful for evaluating the yttrium position in the proposed model. The 'n', and 'k' values for yttrium are determined by using equation 3.38.

$$r = -0.0012(n) + 0.1037 \quad \text{(3.38)}$$

Table 3.6-Part 1 The relationship between log D and pH for Cyanex 272 at 1 M Concentration

Solvent Extractant		**Cyanex 272 (Quinn et al., 2015)**		**Concentration**		**1 M (Quinn et al., 2015)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Ext	**Model**	**MAE**
							-7.60	0.23
1	La						-7.25	
2	Ce	$logD = 3.0075pH - 6.4578$ (Quinn et al., 2015)	0.997	$logD = 3pH - 6.42$ (Quinn et al., 2015)	0.996	-6.42 (Quinn et al., 2015)	-6.90	0.48
3	Pr	$logD = 2.9366pH - 6.0013$ (Quinn et al., 2015)	0.989	$logD = 3pH - 6.18$ (Quinn et al., 2015)	0.987	-6.18 (Quinn et al., 2015)	-6.55	0.37
4	Nd	$logD = 3.0487pH - 6.0688$ (Quinn et al., 2015)	0.993	$logD = 3pH - 6.00$ (Quinn et al., 2015)	0.991	-6.00 (Quinn et al., 2015)	-6.21	0.21

Table 3.6-Part 2 The relationship between log D and pH for Cyanex 272 at 1 M Concentration

Solvent Extractant		**Cyanex 272 (Quinn et al., 2015)**		**Concentration**		**1 M (Quinn et al., 2015)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Ext	**Model**	**MAE**
							-7.60	0.23
5	Pm						-5.86	
6	Sm	$logD = 3.1314pH - 5.0866$ (Quinn et al., 2015)	0.989	$logD = 3pH - 4.80$ (Quinn et al., 2015)	0.983	-4.80 (Quinn et al., 2015)	-5.51	0.71
7	Eu						-5.16	
8	Gd						-4.81	

Table 3.6-Part 3 The relationship between log D and pH for Cyanex 272 at 1 M Concentration

Solvent Extractant		**Cyanex 272 (Quinn et al., 2015)**		**Concentration**		**1 M (Quinn et al., 2015)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Ext	**Model**	**MAE**
							-7.60	0.23
9	Tb	$logD = 3.1307pH - 4.5790$ (Quinn et al., 2015)	0.999	$logD = 3pH - 4.45$ (Quinn et al., 2015)	0.997	-4.45 (Quinn et al., 2015)	-4.46	0.01
10	Dy	$logD = 2.9128pH - 3.9640$ (Quinn et al., 2015)	0.999	$logD = 3pH - 4.10$ (Quinn et al., 2015)	0.978	-4.10 (Quinn et al., 2015)	-4.12	0.02
11	Ho	$logD = 3.3257pH - 4.1030$ (Quinn et al., 2015)	0.999	$logD = 3pH - 3.80$ (Quinn et al., 2015)	0.967	-3.80 (Quinn et al., 2015)	-3.77	0.03
12	Er	$logD = 2.9820pH - 3.3805$ (Quinn et al., 2015)	0.997	$logD = 3pH - 3.40$ (Quinn et al., 2015)	0.997	-3.40 (Quinn et al., 2015)	-3.42	0.02

Table 3.6-Part 4 The relationship between log D and pH for Cyanex 272 at 1 M Concentration

Solvent Extractant		**Cyanex 272 (Quinn et al., 2015)**		**Concentration**		**1 M (Quinn et al., 2015)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Ext	**Model**	**MAE**
							-7.60	0.23
13	Tm						-3.07	
14	Yb	$logD = 2.8084pH - 2.1946$ (Quinn et al., 2015)	0.998	$logD = 3pH - 2.30$ (Quinn et al., 2015)	0.994	-2.30 (Quinn et al., 2015)	-2.72	0.42
15	Lu	$logD = 2.7154pH - 1.9379$ (Quinn et al., 2015)	0.999	$logD = 3pH - 2.12$ (Quinn et al., 2015)	0.990	-2.12 (Quinn et al., 2015)	-2.37	0.25
16	Y	$logD = 2.9833pH - 3.5692$ (Quinn et al., 2015)	0.999	$logD = 3pH - 3.60$ (Quinn et al., 2015)	0.999	-3.60 (Quinn et al., 2015)	-3.62	0.02

Table 3.7 The relationship between ionic radius and the atomic number of lanthanides

No	REE	Ionic radius (nm) (r)	Ionic radius (nm) (Calculated)	n, k
1	La	0.1045 (Pereira et al., 2019)	0.1025	1
2	Ce	0.1010 (Pereira et al., 2019)	0.1013	2
3	Pr	0.0997 (Pereira et al., 2019)	0.1001	3
4	Nd	0.0983 (Pereira et al., 2019)	0.0989	4
5	Pm	0.0970 (Pereira et al., 2019)	0.0977	5
6	Sm	0.0958 (Pereira et al., 2019)	0.0965	6
7	Eu	0.0947 (Pereira et al., 2019)	0.0953	7
8	Gd	0.0938 (Pereira et al., 2019)	0.0941	8
9	Tb	0.0923 (Pereira et al., 2019)	0.0929	9
10	Dy	0.0912 (Pereira et al., 2019)	0.0917	10
11	Ho	0.0901 (Pereira et al., 2019)	0.0905	11
12	Er	0.0890 (Pereira et al., 2019)	0.0893	12
13	Tm	0.0880 (Pereira et al., 2019)	0.0881	13
14	Yb	0.0868 (Pereira et al., 2019)	0.0869	14
15	Lu	0.0861 (Pereira et al., 2019)	0.0857	15
16	Y	0.0900 (Pereira et al., 2019)		11.41

3.6.4 Model description

Since the distribution coefficient of REEs depends on pH, extractant concentration, extractant type, temperature, diluents, diluent type, and phase ratio Equation 3.18 cannot be used to calculate the distribution coefficient. Hence, it was necessary to have at least four experimental data points related to one REE in log D vs. pH plot. First and foremost, we need to investigate the gradient of four data points that are close to 3. The proposed model cannot be used if the gradient of four data points is closer to 2.

As shown in Figure. 3.2 the four steps to determine the entire REE series are as follows:

Step 1. Plot the best fitting curve with gradient 3

Step 2. Determine the intercept in the plot

Step 3. Substitute the intercept (C_n) with a REE number (For example: Tb number is 9)

Step 4. Determine C in the equation and then intercept values for the rest of REEs

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	11.41
REE	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y

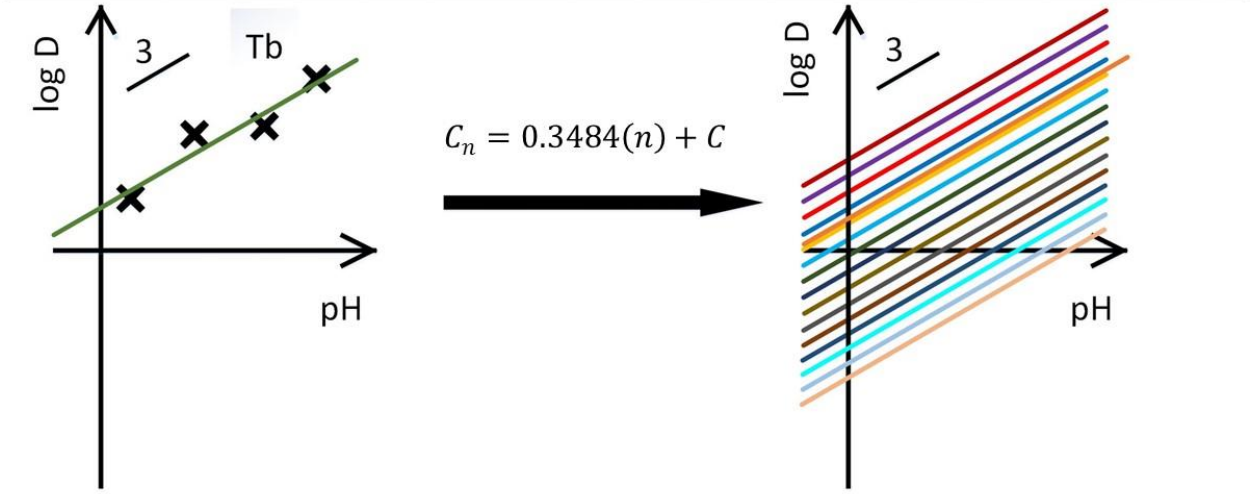

Figure 3.2 Model Description for log D vs pH Plot

3.6.5 Comparison of two extractants in log D vs pH plot

The distribution coefficient relies on the extractant type (Quinn et al., 2015). Some studies focus on two extractants for REEs solvent extraction. Quinn et al. proved that the intercept gap between 1 M Cyanex 572 and 1 M EHEPA was approximately logarithmic 1.05 for cerium (Quinn et al., 2015). Ohto et al. proved that the formed complex between some REEs and EHEHPA was the same complex for the same REEs and D2EHEPA (Ohto et al., 1995).

$$GRD_{pH\ \ Extractant1} = GRD_{pH\ Extractant1} = n^{/} = 3 \quad \text{..... (3.39)}$$

$$C_{pH\ Extractant1} = \frac{m}{2}\log(HR)_2 - \frac{\Delta H^o_{Extractant\ 1}}{2.303 \times R \times T} + \frac{\Delta S^o_{Extractant\ 1}}{2.303 \times R} = \frac{m}{2}\log(HR)_2$$

$$+\log K_{ex\ Extractant1} = \frac{m}{2}\log(HR)_2 - \frac{(\Delta G^o_{Extractant\ 1})}{2.303\times R\times T} \quad (3.40)$$

$$C_{pH\ Extractant2} = \frac{m}{2}\log(HR)_2 - \frac{\Delta H^o_{Extractant\ 2}}{2.303\times R\times T} + \frac{\Delta S^o_{Extractant\ 2}}{2.303\times R} = \frac{m}{2}\log(HR)_2$$

$$+\log K_{ex\ Extractant2} = \frac{m}{2}\log(HR)_2 - \frac{(\Delta G^o_{Extractant\ 2})}{2.303\times R\times T} \quad (3.41)$$

$$\Delta C_{pH\ Extractant} = C_{pH\ Extractant1} - C_{pH\ Extractant2} = -\frac{(\Delta H^o_{Extractant\ 1} - \Delta H^o_{Extractant\ 2})}{2.303\times R\times T} + \frac{(\Delta S^o_{Extractant\ 1} - \Delta S^o_{Extractant\ 2})}{2.303\times R} = \log K_{ex\ Extractant1} - \log K_{ex\ Extractant2} = -\frac{(\Delta G^o_{Extractant\ 1} - \Delta G^o_{Extractant\ 2})}{2.303\times R\times T} \quad (3.42)$$

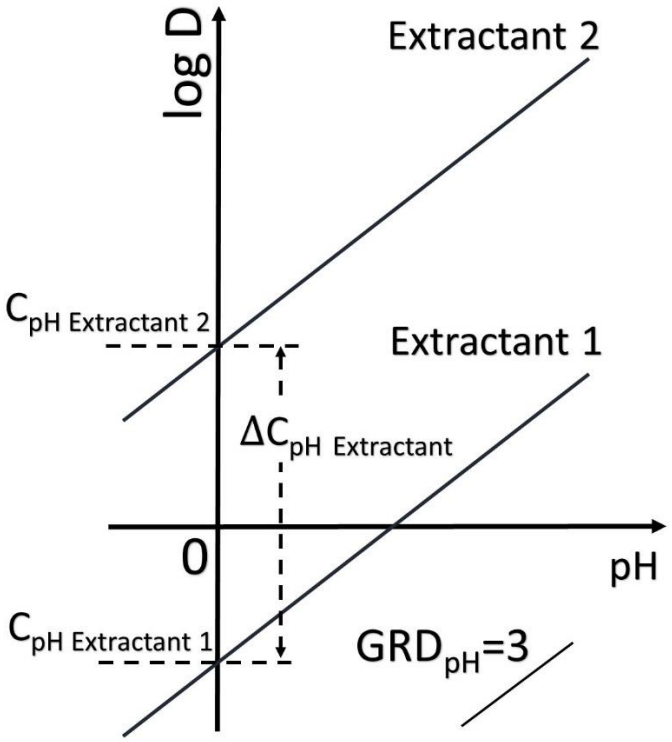

Figure 3.3 The comparison of two extractants for log D vs pH plot

3.7 Effect of Extractant Concentration (log D vs log (H_2R_2))

3.7.1 Comparison of two REEs in log D vs log (H_2R_2) plot

The gradient in the plot log D vs. log (H_2R_2) depends on the nature of the formed complex by the equilibrium reaction. Quinn et al. proved that the gradient was constant for a specific range of

extractant concentration (Quinn et al., 2015). This section is based on the assumption that all REE lines are parallel in log D vs. log (H_2R_2) for a specific extractant concentration range.

$$GRD_{H_2R_2\ REE1} = GRD_{H_2R_2\ REE2} = \frac{m}{2} \quad \text{..... (3.43)}$$

$$C_{H_2R_2\ REE1} = n/pH - \frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R} \quad \text{..... (3.44)}$$

$$C_{H_2R_2\ REE2} = n/pH - \frac{\Delta H^o_{REE\ 2}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 2}}{2.303\times R} \quad \text{..... (3.45)}$$

$$\Delta C_{H_2R_2\ REE} = C_{H_2R_2\ REE1} - C_{H_2R_2\ REE2} = -\frac{(\Delta H^o_{REE\ 1} - \Delta H^o_{REE\ 2})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\ 1} - \Delta S^o_{REE\ 2})}{2.303\times R} =$$

$$logK_{ex\ REE1} - \log K_{exREE\ 2} = -\frac{(\Delta G^o_{REE\ 2} - \Delta G^o_{REE\ 2})}{2.303\times R\times T} \quad \text{..... (3.46)}$$

The above-mentioned equation was modified for any two REEs as shown below,

$$\Delta C^{n-k}_{H_2R_2\ REE} = C_{H_2R_2\ REE\ n} - C_{H_2R_2\ REE\ k} = -\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303\times R} =$$

$$logK_{ex\ REE\ n} - \log K_{exREE\ k} = -\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303\times R\times T} \quad \text{..... (3.47)}$$

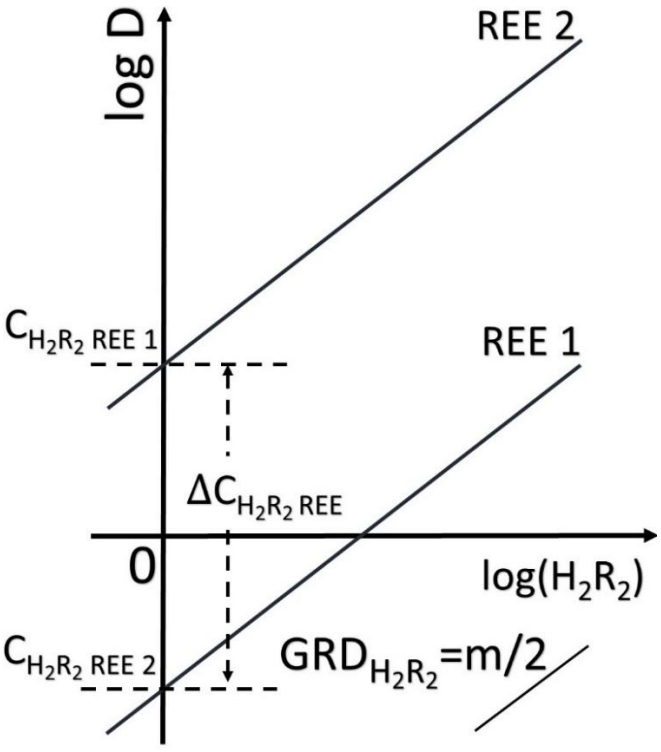

Figure 3.4 The comparison of two adjacent REEs for log D vs log (H_2R_2) plot

Now, comparing Equations 3.34 and 3.46, we see some similarities between the intercept difference from log D vs. pH and log D vs. log (H_2R_2) plot. The certainty of the proposed model applicability for the log D vs. log (H_2R_2) plot was examined by measuring absolute error. As shown in Table 3.8, the mean absolute error between the proposed model and experimental results was very small. Thus, the proposed model can be used for the log D vs. log (H_2R_2) plot to determine the entire REE series.

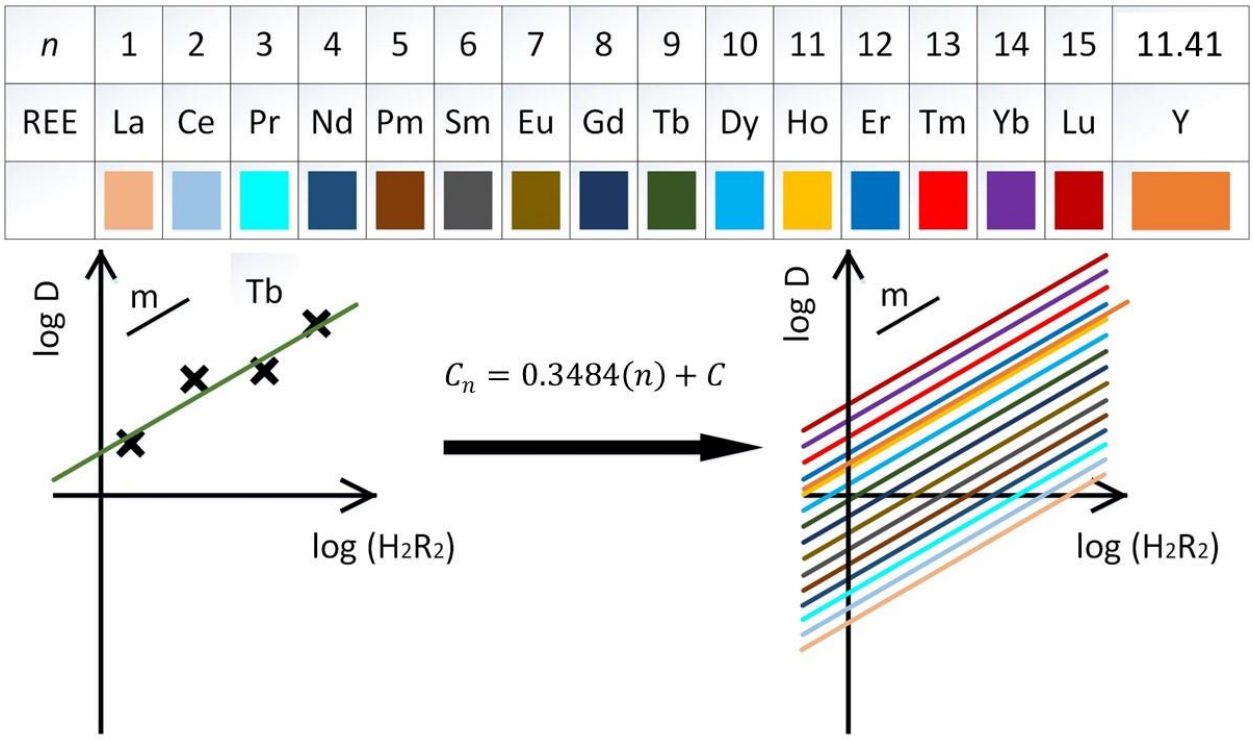

Figure 3.5 Model description for log D vs log (H_2R_2) plot

Table 3.8-Part 1 The relationship between log D and pH for EHEHPA at 1 M Concentration

Solvent Extractant		**EHEHPA (Registered et al., 2007)**		**pH**	**N/A**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model**		
						Ext	**Model**	**MAE**
							-2.36	0.33
1	La						-2.01	
2	Ce						-1.66	
3	Pr	$logD = 3.000\log(H_2R_2) - 1.2500$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2) - 1.25$ (Registered et al., 2007)	1	-1.25 (Registered et al., 2007)	-1.31	0.06
4	Nd	$logD = 3.000\log(H_2R_2) - 1.0000$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2) - 1.00$ (Registered et al., 2007)	1	-1.00 (Registered et al., 2007)	-0.97	0.03

Table 3.8-Part 2 The relationship between log D and pH for EHEHPA at 1 M Concentration

Solvent Extractant		**EHEHPA (Registered et al., 2007)**		**pH**	**N/A**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model**		
						Ext	**Model**	**MAE**
							-2.36	0.33
5	Pm						-0.62	
6	Sm	$logD = 3.000\log(H_2R_2) + 0.0667$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2) + 0.07$ (Registered et al., 2007)	1	0.07 (Registered et al., 2007)	-0.27	0.34
7	Eu	$logD = 3.025\log(H_2R_2) + 0.3417$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2) + 0.34$ (Registered et al., 2007)	1	0.34 (Registered et al., 2007)	0.08	0.26
8	Gd	$logD = 2.975\log(H_2R_2) + 0.6417$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2) + 0.64$ (Registered et al., 2007)	1	0.64 (Registered et al., 2007)	0.43	0.21

Table 3.8-Part 3 The relationship between log D and pH for EHEHPA at 1 M Concentration

Solvent Extractant		**EHEHPA (Registered et al., 2007)**		**pH**	**N/A**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model**		
						Ext	**Model**	**MAE**
							-2.36	0.33
9	Tb						0.78	
10	Dy						1.12	
11	Ho	$logD = 3.000\log(H_2R_2) + 1.9500$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2)$ - 1.95 (Registered et al., 2007)	1	1.95 (Registered et al., 2007)	1.47	0.48
12	Er	$logD = 3.025\log(H_2R_2) + 2.4417$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2)$ - 2.44 (Registered et al., 2007)	1	2.44 (Registered et al., 2007)	1.82	0.62

Table 3.8-Part 4 The relationship between log D and pH for EHEHPA at 1 M Concentration

Solvent Extractant		**EHEHPA (Registered et al., 2007)**		**pH**	**N/A**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model**		
						Ext	**Model**	**MAE**
							-2.36	0.33
13	Tm						2.17	
14	Yb						2.52	
15	Lu						2.87	
16	Y	$logD = 3.000\log(H_2R_2) + 2.2333$ (Registered et al., 2007)	1	$logD = 3.000\log(H_2R_2) + 2.23$ (Registered et al., 2007)	1	2.23 (Registered et al., 2007)	1.62	0.62

3.8 Complex Extraction Equilibrium Equations

The model formulation section was proposed based on an equilibrium reaction, which uses an acidic extractant. It has been proven beyond a doubt that the model was valid for acidic extraction but does not show the model validity for acidic extractant with a media, solvation extractant, and basic extractant. Therefore, an examination of the intercept difference between two adjacent lanthanides in log D vs. pH, and log D vs. log (H_2R_2) was carried out.

3.8.1 Acidic extractants in chloride media

Zhao et al. conducted experiments to study the solvent extraction reaction of REEs with HEHEHP and HEHAMP. Three plots were used to determine the equilibrium equation of an REE reaction with HEHEHP and HEHAMP in chloride media: log D vs. pH, log D vs. log (HEHEHP), and log D vs. log (HEHAMP) (Q. Zhao et al., 2019). The reaction was presented in their paper as follows (Equation 3.48) (Q. Zhao et al., 2019),

$$Ln^{+3}_{(aq)} + (3-n^{/})X^{-}_{(aq)} + m(HEHEHP)_{2(org)} + k(HEHAMP)_{2(org)} \rightarrow Ln[(HEHAMP)_2]_m[(HEHAMP)_2]_k X_{3-n} H_{m+k-n_{(org)}} + nH^{+}_{(aq)} \quad (3.48)$$

$$K_{ex} = \frac{\left[Ln[(HEHAMP)_2]_m[(HEHAMP)_2]_k X_{3-n} H_{m+k-n_{(org)}}\right][H^+]^n}{[Ln^{+3}][(HEHAMP)_2]^m[(HEHAMP)_2]^k[X^-]^{3-n}} \quad (3.49)$$

$$\log K_{ex} = \log D - m\log(HEHEHP)_2 - k\log(HEHAMP)_2 - npH - (3-n)\log(X^-) \quad (3.50)$$

$$\log D = m\log(HEHEHP)_2 + k\log(HEHAMP)_2 + n^{/}pH + \left(3-n^{/}\right)\log(X^-) - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad (3.51)$$

3.8.2 Solvation extractant in nitrate media

Aly et al. used TRPO to measure extraction mechanism of Ce, Yb, and Y. According to their findings, the solvent extraction equilibrium equation was Equation 3.52 (Aly et al., 2016).

$$Ln(NO_3)_2^{+}{}_{(aq)} + mTRPO.H_2O_{\,(Org)} \rightarrow Ln(NO_3)_2(OH)mTRPO.H_2O_{\,(Org)} + n^{/}H^{+}_{(aq)} \quad (3.52)$$

$$K_{ex} = \frac{[Ln(NO_3)_2(OH)mTRPO.H_2O\,][H^+]^{n/}}{[Ln(NO_3)_2{}^+][TRPO.H_2O]^m} \quad \text{(3.53)}$$

$$\log K_{ex} = \log D - m\log(TRPO.H_2O) - n/pH \quad \text{(3.54)}$$

$$\log D = m\log(TRPO.H_2O) + n/pH - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad \text{(3.55)}$$

3.8.3 Basic extractant in chloride media

The liquid-liquid extraction of Nd and Dy by pseudoptotic ionic liquid was studied by Matsumoto et al. (Equation 3.56) (Matsumoto, Yamaguchi, & Tahara, 2020).

$$Ln^{+3}_{(aq)} + nCl^-_{(aq)} + mR_3NH^+R/COO^-_{IL} \rightarrow LnCl_3mR_3NH^+R/COO^-_{IL} \quad \text{(3.56)}$$

$$K_{ex} = \frac{[LnCl_3mR_3NH^+R/COO^-_{IL}]}{[Ln^{+3}][R_3NH^+R/COO^-_{IL}]^m[Cl^-]^n} \quad \text{(3.57)}$$

$$\log K_{ex} = \log D - m\log(R_3NH^+R/COO^-_{IL}) - n\log(Cl^-) \quad \text{(3.58)}$$

$$\log D = m\log(R_3NH^+R/COO^-_{IL}) + n\log(Cl^- - \frac{\Delta H^o}{2.303\times R\times T} + \frac{\Delta S^o}{2.303\times R} \quad \text{(3.59)}$$

Table 3.9 The intercept difference of two adjacent lanthanides for log D vs pH and log D vs log(H_2R_2)

No	log D vs pH			log D vs log (H_2R_2)		
	Gradient	**Intercept**	**Intercept Difference**	**Gradient**	**Intercept**	**Intercept Difference**
1	$n^{/}$	$C_{pH\ REE1} = m\log(HEHEHP)_2 + k\log(HEHAMP)_2 + (3-n)\log(Cl^- - \frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R}$	ΔC_{REE}	m, k	$C_{H_2R_2\ REE1} = k\log(HEHAMP)_2 + n^{/}pH + (3-n^{/})\log(Cl^-) - \frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R}$	ΔC_{REE}
2	$n^{/}$	$C_{pH\ REE1} = m\log(TRPO.H_2O) - \frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R}$	ΔC_{REE}	m	$C_{H_2R_2\ REE1} = n^{/}pH - \frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R}$	ΔC_{REE}
3	N/A	N/A	N/A	m	$C_{H_2R_2\ REE1} = n^{/}\log(Cl^-) - \frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R}$	ΔC_{REE}
4	N/A	N/A	N/A	m	$C_{H_2R_2\ REE1} = -\frac{\Delta H^o_{REE\ 1}}{2.303\times R\times T} + \frac{\Delta S^o_{REE\ 1}}{2.303\times R}$	ΔC_{REE}

3.8.4 Basic extractant in nitrate media

Marcus & Abrahamer studied solvent extraction of Ce, Eu, and Lu using tri-iso-octyl ammonium (Equation 3.60) (Marcus & Abrahamer, 1961).

$$Ln(NO_3)_{3(aq)} + mRNO_{3(org)} \rightarrow R_m Ln(NO_3)_{3+m} \quad (3.60)$$

$$K_{ex} = \frac{[R_m Ln(NO_3)_{3+m}]}{[Ln(NO_3)_3][RNO_3]^m} \quad (3.61)$$

$$\log K_{ex} = \log D - m \log(RNO_3) \quad (3.62)$$

$$\log D = m \log(RNO_3 - \frac{\Delta H^o}{2.303 \times R \times T} + \frac{\Delta S^o}{2.303 \times R} \quad (3.63)$$

As mentioned in Table 3.9, the intercept difference between two adjacent lanthanides is equal to the difference between equilibrium constants of them (Equation 3.64).

$$\Delta C_{REE} = \Delta C_{pH\ REE} = \Delta C_{H_2R_2\ REE} = -\frac{(\Delta H^o_{REE\ 1} - \Delta H^o_{REE\ 2})}{2.303 \times R \times T} + \frac{(\Delta S^o_{REE\ 1} - \Delta S^o_{REE\ 2})}{2.303 \times R} = log K_{ex\ REE\ 1} - \log K_{ex\ REE\ 2} = -\frac{(\Delta G^o_{REE\ 1} - \Delta G^o_{REE\ 2})}{2.303 \times R \times T} \quad (3.64)$$

3.9 Effect of Temperature

As mentioned in the literature review, the distribution coefficient is inversely proportional to temperature. The gradient of some REEs are approximately equal due to standard enthalpy of formation of some REEs are slightly different from each other (Pereira et al., 2019).

$$GRD_{T\ REE1} = -\frac{\Delta H^o_{REE\ 1}}{2.303 \times R} \quad (3.65)$$

$$C_{T\ REE1} = n' pH + \frac{m}{2} \log(HR)_2 + \frac{\Delta S^o_{REE\ 1}}{2.303 \times R} \quad (3.66)$$

$$C_{T\ REE2} = n' pH + \frac{m}{2} \log(HR)_2 + \frac{\Delta S^o_{REE\ 2}}{2.303 \times R} \quad (3.67)$$

$$C_{T\ REE1} - C_{T\ REE2} = \frac{(\Delta S^o_{REE\ 1} - \Delta S^o_{REE\ 2})}{2.303 \times R} \quad (3.68)$$

$$GRD_{T\ REE1} - GRD_{T\ REE2} = -\frac{(\Delta H^o_{REE\ 1} - \Delta H^o_{REE\ 2})}{2.303 \times R} \quad (3.69)$$

$$\frac{GRD_{T\ REE1} - GRD_{T\ REE2}}{T} = -\frac{(\Delta H^o_{REE\ 1} - \Delta H^o_{REE\ 2})}{2.303 \times R \times T} \quad (3.70)$$

$$\frac{GRD_{T\ REE1}-GRD_{T\ REE2}}{T}+C_{T\ REE1}-C_{T\ REE2}=-\frac{(\Delta H^{o}_{REE\ 1}-\Delta H^{o}_{REE\ 2})}{2.303\times R\times T}+\frac{(\Delta S^{o}_{REE\ 1}-\Delta S^{o}_{REE\ 2})}{2.303\times R} \quad (3.71)$$

$$\Delta C_{REE}=\Delta C_{pH\ REE}=\Delta C_{H_2R_2\ REE}=-\frac{(\Delta H^{o}_{REE\ 1}-\Delta H^{o}_{REE\ 2})}{2.303\times R\times T}+\frac{(\Delta S^{o}_{REE\ 1}-\Delta S^{o}_{REE\ 2})}{2.303\times R}=\frac{GRD_{3\ REE\ 1}-GRD_{3\ REE\ 2}}{T}+C_{3\ REE\ 1}-C_{3\ REE\ 2} \quad (3.72)$$

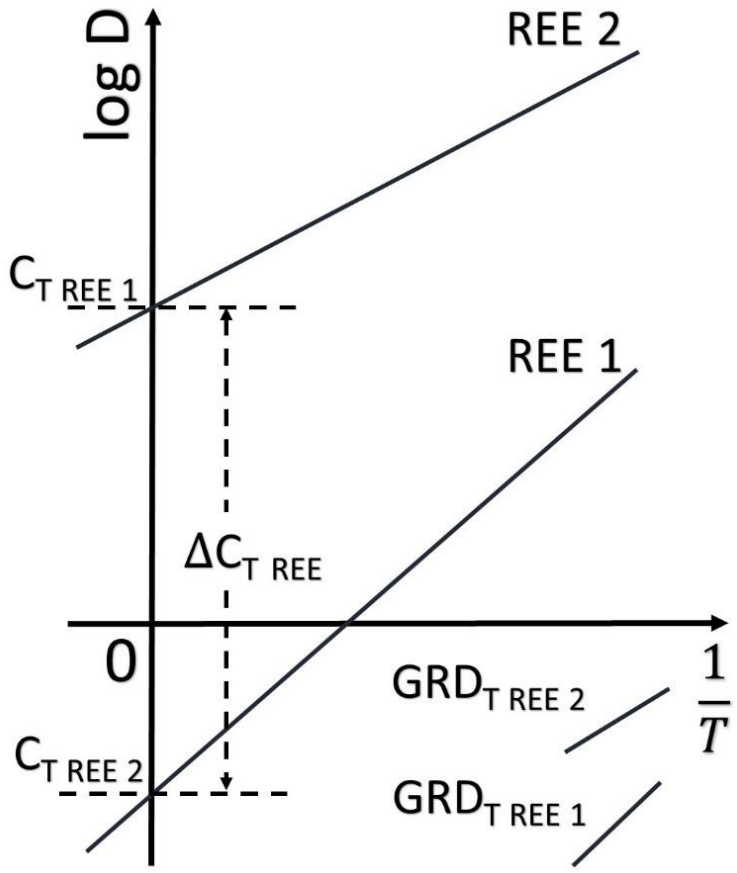

Figure 3.6 The comparison of two adjacent rare earth elements for log D vs 1/T plot

3.10 The Separation Factor

The analysis presented in this section shows that the distribution coefficient of the solvent extraction of REE deviation depends on the equilibrium constant. It is evident that the log value of the equilibrium constant is directly proportional to the Gibbs free energy of formation. That implies the separation factor can be determined using the Gibbs free energy of formation.

$$log(\alpha(REE_1, REE_2)) = log\left(\frac{D_{REE_1}}{D_{REE_2}}\right) \quad (3.73)$$

$$log(\alpha(REE_1, REE_2)) = logD_{REE\ 1} - logD_{REE\ 2} \quad (3.74)$$

$$\log K_{ex\ REE\ 1} = \log D_{REE\ 1} - \frac{m}{2}\log(HR)_2 - n/pH \quad (3.75)$$

$$\log K_{ex\ REE\ 2} = \log D_{REE\ 2} - \frac{m}{2}\log(HR)_2 - n/pH \quad (3.76)$$

$$log\big(\alpha(REE_1, REE_2)\big) = \log D_{REE\ 1} - \log D_{REE\ 2} = \log K_{exREE\ 1} - \log K_{exREE\ 2} \quad (3.77)$$

$$\alpha(REE_1, REE_2) = \frac{D_{REE\ 1}}{D_{REE\ 2}} = \frac{K_{exREE\ 1}}{K_{exREE\ 2}} \quad (3.78)$$

$$logK_{ex\ REE1} - \log K_{ex\ REE\ 2} = -\frac{(\Delta G^o_{REE\ 1} - \Delta G^o_{REE\ 2})}{2.303 \times R \times T} \quad (3.79)$$

$$\alpha(REE_1, REE_2) = \frac{D_{REE\ 1}}{D_{REE\ 2}} = \frac{K_{ex\ REE\ 1}}{K_{ex\ REE\ 2}} = 10^{-\frac{(\Delta G^o_{REE\ 1} - \Delta G^o_{REE\ 2})}{2.303 \times R \times T}} = 10^{-\frac{(\Delta H^o_{REE\ 1} - \Delta H^o_{REE\ 2})}{2.303 \times R \times T}} + \frac{(\Delta S^o_{REE\ 1} - \Delta S^o_{REE\ 2})}{2.303 \times R} \quad (3.80)$$

For any two REEs,

$$\alpha(REE_n, REE_k) = \frac{D_{REE\ n}}{D_{REE\ k}} = \frac{K_{ex\ REE\ n}}{K_{ex\ REE\ k}} = 10^{-\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303 \times R \times T}} = 10^{-\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303 \times R \times T}} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303 \times R} \quad (3.81)$$

The intercept difference between two adjacent lanthanides was calculated as follows (Equation 3.76). A value for the separation factor of any two adjacent lanthanides was calculated using the proposed model.

$$\Delta C_{REE\ Mean} = 0.3484 \quad (3.82)$$

$$\alpha(REE_1, REE_2) = 10^{\Delta C_{REE\ Mean}} = 10^{0.3484} = 2.343668 \quad (3.83)$$

Equation 3.77 can be extended as follows to find the separation factor between any two REEs. Here n>k and the n, and k values are shown in Table 3.7.

$$\alpha(REE_n, REE_k) = 10^{\Delta C_{REE\,Mean}(n-k)} = 10^{0.3484(n-k)} \quad (3.84)$$

3.11 Extraction Efficiency

The proposed model and Equation 2.09 can be utilized to calculate extraction efficiency deviations with pH and extraction concentration. Even though Equation 2.05 is used to determine extraction efficiency, it is better to have an equation to determine the extraction efficiency value of REEs. Let us consider any two REEs with similar solvent extraction conditions (pH, phase ratio, extractant type, extractant concentration, diluent type, diluent concentration, and temperature).

$$D = \left(\frac{E}{100-E}\right) \times PR \quad (3.85)$$

$$\frac{D_{REE\,1}}{D_{REE\,2}} = \left(\frac{E_{REE\,1}}{E_{REE\,2}}\right)\left(\frac{100-E_{REE\,2}}{100-E_{REE\,1}}\right) = \frac{K_{ex\,REE\,1}}{K_{ex\,REE\,2}} = 10^{-\frac{(\Delta G^o_{REE\,1} - \Delta G^o_{REE\,2})}{2.303\times R\times T}} =$$

$$10^{-\frac{(\Delta H^o_{REE\,1} - \Delta H^o_{REE\,2})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\,1} - \Delta S^o_{REE\,2})}{2.303\times R}} \quad (3.86)$$

$$L = \frac{K_{ex\,REE\,1}}{K_{ex\,REE\,2}} = 10^{-\frac{(\Delta G^o_{REE\,1} - \Delta G^o_{REE\,2})}{2.303\times R\times T}} = 10^{-\frac{(\Delta H^o_{REE\,1} - \Delta H^o_{REE\,2})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\,1} - \Delta S^o_{REE\,2})}{2.303\times R}} \quad (3.87)$$

$$\left(\frac{E_{REE\,1}}{E_{REE\,2}}\right)\left(\frac{100-E_{REE\,2}}{100-E_{REE\,1}}\right) = L \quad (3.88)$$

$$E_{REE\,2} = \frac{100\times E_{REE\,1}}{100L - E_{REE\,1}L + E_{REE\,1}} \quad (3.89)$$

Let us consider any two REEs,

$$E_{REE\,n} = \frac{100\times E_{REE\,k}}{100\times \bar{L} - E_{REE\,k}\times \bar{L} + E_{REE\,k}} \quad (3.90)$$

$$\bar{L} = \frac{K_{ex\,REE\,n}}{K_{ex\,REE\,k}} = 10^{-\frac{(\Delta G^o_{REE\,n} - \Delta G^o_{REE\,k})}{2.303\times R\times T}} = 10^{-\frac{(\Delta H^o_{REE\,n} - \Delta H^o_{REE\,k})}{2.303\times R\times T} + \frac{(\Delta S^o_{REE\,n} - \Delta S^o_{REE\,k})}{2.303\times R}} \quad (3.91)$$

$$L' = 10^{\Delta C_{REE\,Mean}} = 10^{0.3484} = 2.343668 \quad (3.92)$$

$$E_{REE\,2} = \frac{100\times E_{REE\,1}}{100\times 2.343668 - E_{REE\,1}\times 2.343668 + E_{REE\,1}} \quad (3.93)$$

Now, comparing Equations 3.83 and 3.84, we can see similarities in Equation 3.93. In other words, Equation 3.93 can be expanded as given in Equation 3.95.

$$L'^{n,k} = 10^{\Delta C_{REE\,Mean(n-k)}} = 10^{0.3484(n-k)} \quad (3.94)$$

$$E_{REE\ 2} = \frac{100 \times E_{REE\ 1}}{100 \times 10^{0.3484(n-k)} - E_{REE\ 1} \times 10^{0.3484(n-k)} + E_{REE\ 1}} \quad \text{..... (3.95)}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Model Performance Evaluation

4.1.1 Effect of pH

The experimental and model prediction values of the distribution coefficient are shown in tables 3.6, A.1, A.4, A.9, and A.18 with their mean absolute error. It is evident that each intercept data point represents four or more logarithmic values of the distribution coefficients. As can be seen, the intercepts of log D vs. pH decrease with an increasing ionic radius. Moreover, the results of the proposed model and experimental result of Cyanex 272, Cyanex 572, EHEPA, Cyanex 272, and Cyanex 301 are compared in Figure 4.1. Clearly, the model is capable of predicting the intercepts of REEs in log D vs. pH plot.

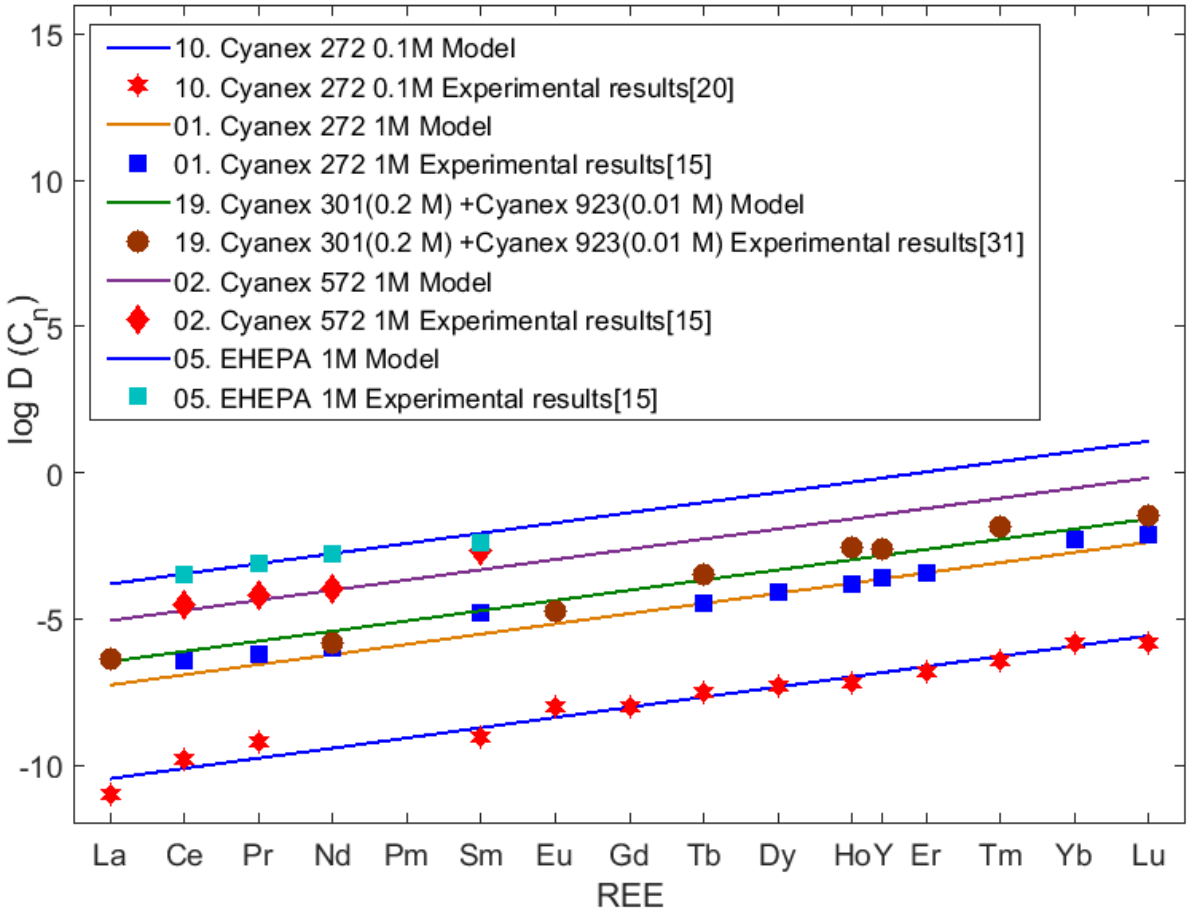

Figure 4.1 The relationship between rare earth elements and C_n for the model prediction and experimental results for log D vs pH plot

4.1.2 Effect of extractant concentrations

Similarities were found between the REEs intercept deviation in log D vs. log (H_2R_2) and log D vs. pH, which increases with an increasing ionic radius. As mentioned in the literature review, the gradient of log D vs. log (H_2R_2) is valid only for a specific range of extractant concentrations (Quinn et al., 2015). However, the model is valid for any gradient value. A graphical examination of the intercept values experimental and calculated using the model in log D vs. log (H_2R_2) plot are presented in Figure 4.2. The proposed model slightly deviates from the experimental results, as shown.

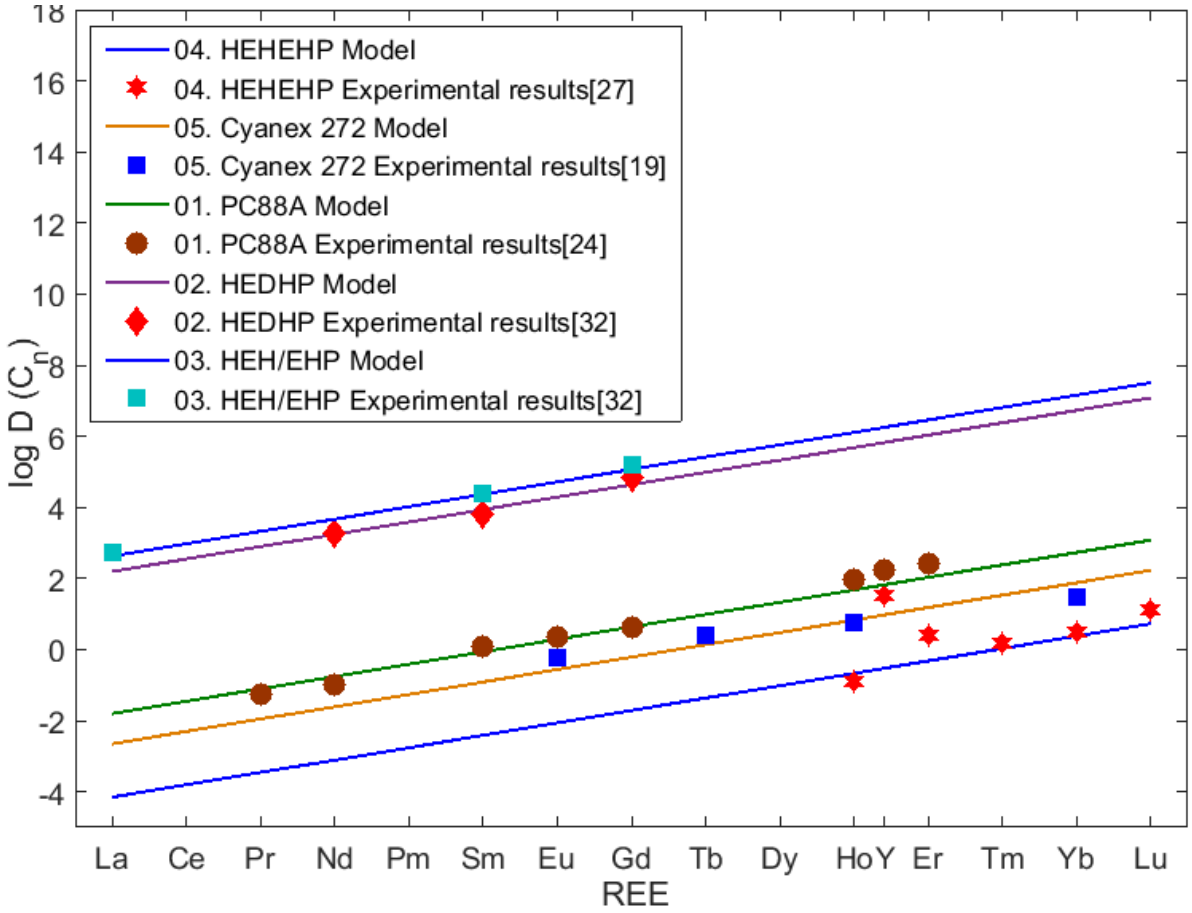

Figure 4.2 The relationship between rare earth elements and C_n for the model prediction and experimental results for log D vs log (H_2R_2) plot

4.1.3 Effect of the equilibrium constant

As mentioned in the effect of extractant sub section, the intercept difference between any two adjacent REEs is equal to the difference of their equilibrium constants. The proposed model can be used to calculate the equilibrium constant. Turanov et al. carried out research to determine the equilibrium constants of some REEs solvent extraction with TODGA. Their equilibrium extraction reaction is shown in Equation 4.02 (Turanov et al., 2017). Let us assume that all parameters (extractant type, pH, temperature phase ratio, diluent, and diluent concentration) are identical values for two adjacent REEs. The intercept difference between two adjacent REEs in the log D vs. log (H_2R_2) plot is shown in Equation 4.03. The proposed model can be used for predicting the logarithmic value of the distribution. This comparison indicates that the model is capable of predicting the equilibrium constant.

$$Ln^{+3}_{(aq)} + 3Tf_2N^-{}_{(Org)} + 3R_{(org)} \rightarrow LnR_2(Tf_2N)_{3(Org)} \ldots\ldots\ldots\ldots\ldots\ldots (4.01)$$

$$K_{ex} = \frac{[LnR_2(Tf_2N)_{3(Org)}]}{\left[Ln^{+3}_{(aq)}\right]\left[Tf_2N^-{}_{(Org)}\right]^3[R_{(org)}]^3} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.02)$$

$$log\, K_{ex} = log\, D - 3\, log(Tf_2N^-) - 3\, log(R) \ldots\ldots\ldots\ldots\ldots\ldots (4.03)$$

$$log\, D = 3\, log(Tf_2N^-) + log\, K_{ex} + 3\, log(R) \ldots\ldots\ldots\ldots\ldots\ldots (4.04)$$

$$\Delta C'_{2\,REE} = C'_{2\,REE1} - C'_{2\,REE2} = logK'_{ex\,REE1} - \log K'_{ex\,REE1} \ldots\ldots\ldots\ldots\ldots\ldots (4.05)$$

Table 4.1 The relationship between equilibrium constant experimental results and model prediction for lanthanides

No	REE	$logK_{ex}$	Model
1	La	20.39 (Turanov et al., 2017)	20.3900
2	Ce	21.30 (Turanov et al., 2017)	20.7599
3	Pr	21.94 (Turanov et al., 2017)	21.1298
4	Nd	22.53 (Turanov et al., 2017)	21.4997
5	Sm	23.54 (Turanov et al., 2017)	22.2395
6	Eu	23.68 (Turanov et al., 2017)	22.6094
7	Gd	23.86 (Turanov et al., 2017)	22.9793
8	Tb	24.18 (Turanov et al., 2017)	23.3492
9	Dy	24.36 (Turanov et al., 2017)	23.7191
10	Ho	24.48 (Turanov et al., 2017)	24.089
11	Er	24.56 (Turanov et al., 2017)	24.4589
12	Tm	24.55 (Turanov et al., 2017)	24.8288
13	Yb	24.51 (Turanov et al., 2017)	25.1987
14	Lu	24.57 (Turanov et al., 2017)	25.5686

Table 4.2-Part 1 The separation factors prediction from the proposed model

	La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Ln**
La	1.00	2.23	4.98	11.10	24.75	55.21	123.14	274.66	La/Ln
Ce		1.00	2.23	4.98	11.10	24.75	55.21	123.14	Ce/Ln
Pr			1.00	2.23	4.98	11.10	24.75	55.21	Pr/Ln
Nd				1.00	2.23	4.98	11.10	24.75	Nd/Ln
Pm					1.00	2.23	4.98	11.10	Pm/Ln
Sm						1.00	2.23	4.98	Sm/Ln
Eu							1.00	2.23	Eu/Ln
Gd								1.00	Gd/Ln
Tb									Tb/Ln
Dy									Dy/Ln
Ho									Ho/Ln
Er									Er/Ln
Tm									Tm/Ln
Yb									Yb/Ln
Lu									Lu/Ln

Table 4.2-Part 2 The separation factors prediction from the proposed model

	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Ln
La	612.63	1366.47	3047.89	6798.29	15163.52	33822.06	75439.71	4234.9	La/Ln
Ce	274.66	612.63	1366.47	3047.89	6798.29	15163.52	33822.06	1898.6	Ce/Ln
Pr	123.14	274.66	612.63	1366.47	3047.89	6798.29	15163.52	851.2	Pr/Ln
Nd	55.21	123.14	274.66	612.63	1366.47	3047.89	6798.29	381.6	Nd/Ln
Pm	24.75	55.21	123.14	274.66	612.63	1366.47	3047.89	171.1	Pm/Ln
Sm	11.10	24.75	55.21	123.14	274.66	612.63	1366.47	76.7	Sm/Ln
Eu	4.98	11.10	24.75	55.21	123.14	274.66	612.63	34.4	Eu/Ln
Gd	2.23	4.98	11.10	24.75	55.21	123.14	274.66	15.4	Gd/Ln
Tb	1.00	2.23	4.98	11.10	24.75	55.21	123.14	6.9	Tb/Ln
Dy		1.00	2.23	4.98	11.10	24.75	55.21	3.1	Dy/Ln
Ho			1.00	2.23	4.98	11.10	24.75	1.4	Ho/Ln
Er				1.00	2.23	4.98	11.10	0.6	Er/Ln
Tm					1.00	2.23	4.98	0.3	Tm/Ln
Yb						1.00	2.23	0.1	Yb/Ln
Lu							1.00	0.1	Lu/Ln

4.2 The Separation Factor

The present study discovered a separation factor table as mentioned in Table 4.2. According to this model, the separation factor of two adjacent lanthanides is 2.34. However, many experimental results suggested that two separation factors are not equal (Ohto et al., 1995). As seen in Table 4.2, the highest values of lanthanides separation factor occurred at Lu. Nevertheless, the highest separation factor yttrium cannot be found at Lu. The reason behind this is due to the yttrium position, which is between Ho and Er.

4.3 Validity Range

The proposed model is based on an experimental data set. Most of experimental results were carried out with a phase ratio of 1 or higher (organic phase: aqueous phase =1:1). Hence, the proposed model cannot be used to predict a phase ratio lower than 1.

4.3.1 log D vs pH plot

Using the model, the distribution coefficient prediction of REEs can be carried out of pH range as mentioned in Table 4.3. Kumari et al. proved that the best equilibration time is 5 minutes. That being said, anything lower than this reduces extraction efficiency, while values higher than that have an extraction efficiency that remains constant (Kumari et al., 2019).

Table 4.3 The proposed model validity range for log D vs. pH plot and log D vs log (H_2R_2) plot

No	Effective parameter	Range
1	Extractant concentration	$C > 0.1$ M
2	pH	$-2 < pH < 4$
3	Equilibration time	$t > 5$ min
4	Phase ratio	1/PR≥1

4.3.2 log D vs log(H_2R_2) plot

According to the findings of Quinn et al., the gradients of log D vs. log (H_2R_2) are valid for a specific concentration range (Quinn et al., 2015). Therefore, the proposed model is valid only for

a particular range of concentrations. Even though the present work discussed intercept in log D vs. log (H_2R_2) (the log D value where log (H_2R_2)=0), some experimental results are not valid at log (H_2R_2)=0 (Quinn et al., 2015).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A model was proposed to predict the entire lanthanides series and yttrium in the log D vs. pH plot. The proposed model was tested for log D vs. log (H_2R_2) plot, and it was found that the model can be utilized to predict the entire REE series in log D vs. log (H_2R_2) plot. The intercept difference of any two REEs in log D vs. pH and log D vs. log (H_2R_2) plots is equal to 0.3484. Furthermore, it is evident that the equilibrium constant value difference of two adjacent lanthanides is directly proportional to the difference in the standard Gibbs free energy of formation. The separation factor between two REEs can be calculated by using the equilibrium constant of them. It was found that the separation factor depends on the same factors that the equilibrium constant depends on, such as temperature, extractant concentration, extractant type, and REEs concentration. The present study was discovered as four models given below (Table 5.1 and Table 5.2),

Table 5.1 Correlations based on the intercept difference of any two REEs for log D vs. pH and log D vs log (H_2R_2)

No	Description	Theoretical model	Numerical Model
1	The intercept difference of REEs in log D vs pH plot	$\Delta C_{pH\ REE\ n,k} = C_{pH\ REE\ n} - C_{pH\ REE\ k} = -\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303 \times R \times T} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303 \times R} = logK_{ex\ REE\ n} - \log K_{ex\ REE\ k} = -\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303 \times R \times T}$	$\Delta C_{pH\ REE\ n,k} = 0.3484(n-k)$
2	The intercept difference of REEs in log D vs log(H_2R_2) plot	$\Delta C_{H_2R_2\ REE\ n,k} = C_{H_2R_2\ REE\ n} - C_{H_2R_2\ REE\ k} = -\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303 \times R \times T} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303 \times R} = logK_{ex\ REE\ n} - \log K_{ex\ REE\ k} = -\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303 \times R \times T}$	$\Delta C_{H_2R_2\ REE\ n,k} = 0.3484(n-k)$
		Here n, and k are atomic numbers of REEs	Here n, and k values are tabulated in Table 3.7

Table 5.2-Correlations for the separation factor and extraction efficiency

No	Description	Theoretical model	Numerical Model
3	The separation factor	$\alpha(REE_n, REE_k) = \frac{D_{REE\ n}}{D_{REE\ k}} = \frac{K_{ex\ REE\ n}}{K_{ex\ REE\ k}} = 10^{-\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303 \times R \times T}} = 10^{-\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303 \times R \times T}} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303 \times R}$	$\alpha(REE_n, REE_k) = 10^{0.3484(n-k)}$
4	Extraction efficiency	$E_{REE\ n} = \frac{100 \times E_{REE\ k}}{100L - E_{REE\ k}L + E_{REE\ k}}$, $L = \frac{K_{ex\ REE\ n}}{K_{ex\ REE\ k}} = 10^{-\frac{(\Delta G^o_{REE\ n} - \Delta G^o_{REE\ k})}{2.303 \times R \times T}} = 10^{-\frac{(\Delta H^o_{REE\ n} - \Delta H^o_{REE\ k})}{2.303 \times R \times T}} + \frac{(\Delta S^o_{REE\ n} - \Delta S^o_{REE\ k})}{2.303 \times R}$	$E_{REE\ 2} = \frac{100 \times E_{REE\ 1}}{100 \times 10^{0.3484(n-k)} - E_{REE\ 1} \times 10^{0.3484(n-k)} + E_R}$
		Here n, and k are atomic numbers of REEs	Here n, and k values are tabulated in Table 3.7

5.2 Recommendation

The present study focusses on the effective parameters for REE solvent extraction such as pH, extractant concentration, and temperature. However, the effects of phase ratio and equilibration time have not been studied in-depth. It is essential to determine the distribution coefficient deviation with the phase ratio. Most REEs minerals consist of only REEs. However, scrap metals contain many other elements along with REEs. Hence, it is necessary to carry out experimental studies that examine the distribution coefficient deviation with pH and log (H_2R_2) using scrap metals.

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APPENDIX A

Table A.1-Part A Relation between log D and pH for Cyanex 572 at 1 M Concentration

Solvent Extractant		**Cyanex 572**		**Concentration**	**1 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-5.40	0.26
1	La						-5.05	
2	Ce	$logD = 3.025pH - 4.5458$(Quinn et al., 2015)	1.000	$logD = 3pH - 4.5$ (Quinn et al., 2015)	1.000	-4.50(Quinn et al., 2015)	-4.70	0.20
3	Pr	$logD = 3.050pH - 4.2417$(Quinn et al., 2015)	0.999	$logD = 3pH - 4.2$(Quinn et al., 2015)	1.000	-4.20(Quinn et al., 2015)	-4.35	0.15
4	Nd	$logD = 3.050pH - 4.0750$(Quinn et al., 2015)	1.000	$logD = 3pH - 3.97$ (Quinn et al., 2015)	1.000	-3.97(Quinn et al., 2015)	-4.01	0.04

Table A.1-Part B Relation between log D and pH for Cyanex 572 at 1 M Concentration

Solvent Extractant		**Cyanex 572**		**Concentration**	**1 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-5.40	0.26
5	Pm						-3.66	
6	Sm	$logD = 3.300pH - 3.2500$(Quinn et al., 2015)	1.000	$logD = 3pH - 2.65$ (Quinn et al., 2015)	0.990	-2.65(Quinn et al., 2015)	-3.31	0.66
7	Eu						-2.96	
8	Gd						-2.61	
9	Tb						-2.26	
10	Dy						-1.92	
11	Ho						-1.57	
12	Er						-1.22	
13	Tm						-0.87	
14	Yb						-0.52	
15	Lu						-0.17	
16	Y						-1.42	

Table A.2-Part A Relation between log D and pH for D2EHEPA at 1.56 M Concentration

Solvent Extractant		**D2EHEPA**		**Concentration**		**1 .56 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.65	0.35
1	La	$logD = 3.0000pH -$ 4.1590(Ohto et al., 1995)	1.000	$logD = 3pH -$ 4.16(Ohto et al., 1995)	0.994	-4.16(Ohto et al., 1995)	-4.30	0.14
2	Ce	$logD = 3.0000pH -$ 3.0890(Ohto et al., 1995)	1.000	$logD = 3pH -$ 3.09(Ohto et al., 1995)	0.994	-3.09(Ohto et al., 1995)	-3.95	0.86
3	Pr	$logD = 3.0250pH -$ 3.7211(Ohto et al., 1995)	1.000	$logD = 3pH -$ 3.72(Ohto et al., 1995)	0.996	-3.72(Ohto et al., 1995)	-3.60	0.12
4	Nd	$logD = 2.9488pH -$ 3.4088(Ohto et al., 1995)	1.000	$logD = 3pH -$ 3.25(Ohto et al., 1995)	0.994	-3.25(Ohto et al., 1995)	-3.26	0.01
5	Pm						-2.91	
6	Sm	$logD = 2.9727pH -$ 2.9385(Ohto et al., 1995)	1.000	$logD = 3pH -$ 3.28(Ohto et al., 1995)	0.991	-3.28(Ohto et al., 1995)	-2.56	0.72
7	Eu						-2.21	
8	Gd	$logD = 2.9336pH -$ 2.5714(Ohto et al., 1995)	1.000	$logD = 3pH -$ 2.71(Ohto et al., 1995)	0.996	-2.71(Ohto et al., 1995)	-1.86	0.85

Table A.2-Part B Relation between log D and pH for D2EHEPA at 1.56 M Concentration

Solvent Extractant		**D2EHEPA**		**Concentration**		**1 .56 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.65	0.35
9	Tb						-1.51	
10	Dy						-1.17	
11	Ho	$logD = 3.0000pH - 0.8000$(Ohto et al., 1995)	1.000	$logD = 3pH - 0.80$(Ohto et al., 1995)	0.994	-0.80(Ohto et al., 1995)	-0.82	0.02
12	Er	$logD = 2.9974pH - 0.3979$(Ohto et al., 1995)	1.000	$logD = 3pH - 0.41$(Ohto et al., 1995)	0.996	-0.41(Ohto et al., 1995)	-0.47	0.06
13	Tm						-0.12	
14	Yb						0.23	
15	Lu						0.58	
16	Y						-0.67	

Table A.3- Part A Relation between log D and pH for EHEHPA at 1.61 M concentration

Solvent Extractant		**EHEHPA**		**Concentration**		**1 .61 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.90	0.20
1	La	$logD = 2.9988pH -$ 4.2987(Ohto et al., 1995)	1.000	$logD = 3pH - 4.17$ (Ohto et al., 1995)	0.999	-4.17(Ohto et al., 1995)	-4.55	0.38
2	Ce	$logD = 2.9607pH -$ 3.7880(Ohto et al., 1995)	1.000	$logD = 3pH - 3.80$ (Ohto et al., 1995)	0.999	-3.80(Ohto et al., 1995)	-4.20	0.40
3	Pr	$logD = 3.0000pH -$ 3.7010(Ohto et al., 1995)	1.000	$logD = 3pH - 3.72$(Ohto et al., 1995)	0.999	-3.70(Ohto et al., 1995)	-3.85	0.15
4	Nd	$logD = 3.0017pH -$ 3.5000(Ohto et al., 1995)	1.000	$logD = 3pH - 3.50$ (Ohto et al., 1995)	0.999	-3.50(Ohto et al., 1995)	-3.51	0.01
5	Pm						-3.16	
6	Sm	$logD = 2.9568pH -$ 2.8279(Ohto et al., 1995)	1.000	$logD = 3pH - 2.82$ (Ohto et al., 1995)	0.999	-2.82(Ohto et al., 1995)	-2.81	0.01
7	Eu						-2.46	
8	Gd	$logD = 2.9336pH -$ 2.3040(Ohto et al., 1995)	1.000	$logD = 3pH - 2.31$(Ohto et al., 1995)	0.999	-2.31(Ohto et al., 1995)	-2.11	0.20

Table A.3- Part B Relation between log D and pH for EHEHPA at 1.61 M concentration

Solvent Extractant		**EHEHPA**		**Concentration**		**1 .61 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.90	0.20
9	Tb						-1.76	
10	Dy						-1.42	
11	Ho	$logD = 3.0000pH - 0.7970$(Ohto et al., 1995)	1.000	$logD = 3pH - 0.92$ (Ohto et al., 1995)	0.999	-0.92(Ohto et al., 1995)	-1.07	0.14
12	Er	$logD = 2.9974pH - 0.3979$(Ohto et al., 1995)	1.000	$logD = 3pH - 0.45$(Ohto et al., 1995)	0.999	-0.45(Ohto et al., 1995)	-0.72	0.27
13	Tm						-0.37	
14	Yb						-0.02	
15	Lu						0.33	
16	Y						-0.92	

Table A.4- Part A Relation between log D and pH for EHEPA at 1 M Concentration

Solvent Extractant		**EHEPA**		**Concentration**	**1 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.15	0.09
1	La						-3.80	
2	Ce	$logD = 3.2258pH - 3.8387$(Quinn et al., 2015)	1.000	$logD = 3pH - 3.45$ (Quinn et al., 2015)	0.994	-3.45(Quinn et al., 2015)	-3.45	0.00
3	Pr	$logD = 3.1914pH - 3.4680$(Quinn et al., 2015)	1.000	$logD = 3pH - 3.09$(Quinn et al., 2015)	0.996	-3.09(Quinn et al., 2015)	-3.10	0.01
4	Nd	$logD = 3.1818pH - 3.3681$(Quinn et al., 2015)	1.000	$logD = 3pH - 2.78$ (Quinn et al., 2015)	0.994	-2.78(Quinn et al., 2015)	-2.76	0.02
5	Pm						-2.41	
6	Sm	$logD = 3.1914pH - 2.5212$(Quinn et al., 2015)	1.000	$logD = 3pH - 2.39$ (Quinn et al., 2015)	0.992	-2.39(Quinn et al., 2015)	-2.06	0.33
7	Eu						-1.71	
8	Gd						-1.36	

Table A.4- Part B Relation between log D and pH for EHEPA at 1 M Concentration

Solvent Extractant		**EHEPA**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.15	0.09
9	Tb						-1.01	
10	Dy						-0.67	
11	Ho						-0.32	
12	Er						0.03	
13	Tm						0.38	
14	Yb						0.73	
15	Lu						1.08	
16	Y						-0.17	

Table A.5-Part A Relation between log D and pH for Cyanex 272 at 0.1 M Concentration

Solvent Extractant		**Cyanex 272**		**Concentration**	**0.1 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-11.00	0.56
1	La	$logD = 3.2900pH - 13.05$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 12.4$(Komatsu & Freiser, 1989)	0.990	-12.40(Komatsu & Freiser, 1989)	-10.65	1.75
2	Ce						-10.30	
3	Pr	$logD = 2.7800pH - 9.280$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 9.60$(Komatsu & Freiser, 1989)	0.994	-9.60(Komatsu & Freiser, 1989)	-9.95	0.35
4	Nd						-9.61	
5	Pm						-9.26	
6	Sm						-8.91	
7	Eu	$logD = 2.8600pH - 8.080$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 8.00$ (Komatsu & Freiser, 1989)	0.991	-8.00(Komatsu & Freiser, 1989)	-8.56	0.56
8	Gd						-8.21	

Table A.5-Part B Relation between log D and pH for Cyanex 272 at 0.1 M Concentration

Solvent Extractant		**Cyanex 272**		**Concentration**		**0.1 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-11.00	0.56
9	Tb						-7.86	
10	Dy						-7.52	
11	Ho	$logD = 2.9700pH - 7.100$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 7.20$ (Komatsu & Freiser, 1989)	0.999	-7.20(Komatsu & Freiser, 1989)	-7.17	0.03
12	Er						-6.82	
13	Tm						-6.47	
14	Yb	$logD = 2.9700pH - 5.900$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 6.00$ (Komatsu & Freiser, 1989)	1.000	-6.00(Komatsu & Freiser, 1989)	-6.12	0.12
15	Lu						-5.77	
16	Y						-7.02	

Table A.6-Part A Relation between log D and pH for Cyanex 272 at 0.1 M concertation with TOPO at 0.01 M concentration

Solvent Extractant		**Cyanex 272 with TOPO**		**Concentration**		**0.1 M Cyanex 272 and 0.01 M TOPO**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							<u>-10.20</u>	<u>0.32</u>
1	La	$logD = 2.69pH - 8.90$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 9.51$ (Komatsu & Freiser, 1989)	0.989	-9.51(Komatsu & Freiser, 1989)	-9.85	0.34
2	Ce						-9.50	
3	Pr	$logD = 2.90pH - 8.56$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 8.40$(Komatsu & Freiser, 1989)	0.992	-8.40(Komatsu & Freiser, 1989)	-9.15	0.75
4	Nd						-8.81	
5	Pm						-8.46	
6	Sm						-8.11	
7	Eu	$logD = 3.02pH - 7.30$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 7.60$ (Komatsu & Freiser, 1989)	0.994	-7.60(Komatsu & Freiser, 1989)	-7.76	0.16
8	Gd						-7.41	

Table A.6-Part B Relation between log D and pH for Cyanex 272 at 0.1 M concentration with TOPO at 0.01 M concentration

Solvent Extractant		**Cyanex 272 with TOPO**		**Concentration**		**0.1 M Cyanex 272 and 0.01 M TOPO**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-10.20	0.32
9	Tb						-7.06	
10	Dy						-6.72	
11	Ho	$logD = 3.12pH - 6.50$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 6.50$ (Komatsu & Freiser, 1989)	0.995	-6.50(Komatsu & Freiser, 1989)	-6.37	0.13
12	Er						-6.02	
13	Tm						-5.67	
14	Yb	$logD = 2.81pH - 4.75$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 5.12$ (Komatsu & Freiser, 1989)	0.996	-5.12(Komatsu & Freiser, 1989)	-5.32	0.20
15	Lu						-4.97	
16	Y						-6.22	

Table A.7-Part A Relation between log D and pH for Cyanex 272 at 0.1 M Concentration

Solvent Extractant		**Cyanex 272 with ClO4**		**Concentration**	**0.1 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-11.40	0.47
1	La	$logD = 3.14pH - 12.53$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 12.0$ (Komatsu & Freiser, 1989)	0.994	-12.00(Komatsu & Freiser, 1989)	-11.05	0.95
2	Ce						-10.70	
3	Pr	$logD = 3.13pH - 10.64$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 10.3$(Komatsu & Freiser, 1989)	0.998	-10.30(Komatsu & Freiser, 1989)	-10.35	0.05
4	Nd						-10.01	
5	Pm						-9.66	
6	Sm						-9.31	
7	Eu	$logD = 3.07pH - 8.910$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 8.80$ (Komatsu & Freiser, 1989)	0.999	-8.80(Komatsu & Freiser, 1989)	-8.96	0.16
8	Gd						-8.61	

Table A.7-Part B Relation between log D and pH for Cyanex 272 at 0.1 M Concentration

Solvent Extractant		**Cyanex 272 with ClO4**		**Concentration**	**0.1 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-11.40	0.47
9	Tb						-8.26	
10	Dy						-7.92	
11	Ho	$logD = 2.81pH - 6.650$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 6.90$ (Komatsu & Freiser, 1989)	0.995	-6.90(Komatsu & Freiser, 1989)	-7.57	0.67
12	Er						-7.22	
13	Tm						-6.87	
14	Yb	$logD = 2.81pH - 6.650$(Komatsu & Freiser, 1989)	1.000	$logD = 3pH - 6.90$ (Komatsu & Freiser, 1989)	0.997	-6.00(Komatsu & Freiser, 1989)	-6.52	0.52
15	Lu						-6.17	
16	Y						-7.42	

Table A.8-Part A Relation between log D and pH for TBDGA at 0.25 M Concentration

Solvent Extractant		**TBDGA**		**Concentration**	**0.25 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-2.00	0.24
1	La	$logD = 3.2900pH - 13.050$(D. F. Peppard et al., 1958)	1.000	$logD = 3pH - 1.48$ (D. F. Peppard et al., 1958)	0.990	-1.48(D. F. Peppard et al., 1958)	-1.65	0.17
2	Ce	$logD = 2.8600pH - 8.0800$(D. F. Peppard et al., 1958)	1.000	$logD = 3pH - 1.28$ (D. F. Peppard et al., 1958)	0.991	-1.28(D. F. Peppard et al., 1958)	-1.30	0.02
3	Pr	$logD = 2.7800pH - 9.2800$(D. F. Peppard et al., 1958)	1.000	$logD = 3pH - 1.24$(D. F. Peppard et al., 1958)	0.994	-1.24(D. F. Peppard et al., 1958)	-0.95	0.29
4	Nd	$logD = 2.8600pH - 8.0800$(D. F. Peppard et al., 1958)	1.000	$logD = 3pH - 1.08$(D. F. Peppard et al.,	0.991	-1.08(D. F. Peppard et al., 1958)	-0.61	0.47
5	Pm						-0.26	
6	Sm						0.09	
7	Eu						0.44	
8	Gd						0.79	

Table A.8-Part B Relation between log D and pH for TBDGA at 0.25 M Concentration

Solvent Extractant		**TBDGA**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-2.00	0.24
9	Tb						1.14	
10	Dy						1.48	
11	Ho						1.83	
12	Er						2.18	
13	Tm						2.53	
14	Yb						2.88	
15	Lu						3.23	
16	Y						1.98	

Table A.9-Part A Relation between log D and pH for Cyanex 272 at 0.1 M Concentration

Solvent Extractant		**Cyanex 272**		**Concentration**		**0.1 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-11.10	0.33
1	La	$logD = 2.65pH - 10.05$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 11.0$(L. I. Deqian, 2017)	0.983	-11.0(L. I. Deqian, 2017)	-10.75	0.25
2	Ce	$logD = 2.56pH - 8.860$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 9.80$(L. I. Deqian, 2017)	0.978	-9.80(L. I. Deqian, 2017)	-10.40	0.60
3	Pr	$logD = 2.50pH - 8.200$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 9.20$(L. I. Deqian, 2017)	0.972	-9.20(L. I. Deqian, 2017)	-10.05	0.85
4	Nd	$logD = 2.45pH - 7.875$(L. I. Deqian, 2017)	1.000	$logD = 2pH - 7.20$(L. I. Deqian, 2017)	0.943		-9.71	
5	Pm						-9.36	
6	Sm	$logD = 2.75pH - 7.875$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 8.60$(L. I. Deqian, 2017)	0.990	-9.02(L. I. Deqian, 2017)	-9.01	0.01
7	Eu	$logD = 2.80pH - 7.725$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 8.00$(L. I. Deqian, 2017)	0.994	-8.00(L. I. Deqian, 2017)	-8.66	0.66
8	Gd	$logD = 2.70pH - 7.375$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 7.98$(L. I. Deqian, 2017)	0.989	-7.98(L. I. Deqian, 2017)	-8.31	0.33

Table A.9-Part B Relation between log D and pH for Cyanex 272 at 0.1 M Concentration

Solvent Extractant		**Cyanex 272**		**Concentration**		**0.1 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-11.10	0.33
9	Tb	$logD = 2.70pH - 6.900$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 7.50$(L. I. Deqian, 2017)	0.990	-7.50(L. I. Deqian, 2017)	-7.96	0.46
10	Dy	$logD = 2.75pH - 6.750$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 7.30$(L. I. Deqian, 2017)	0.991	-7.30(L. I. Deqian, 2017)	-7.62	0.32
11	Ho	$logD = 2.80pH - 6.525$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 7.20$(L. I. Deqian, 2017)	0.991	-7.20(L. I. Deqian, 2017)	-7.27	0.07
12	Er	$logD = 2.75pH - 6.150$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 7.80$(L. I. Deqian, 2017)	0.990	-6.80(L. I. Deqian, 2017)	-6.92	0.12
13	Tm	$logD = 3.00pH - 6.400$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 6.40$(L. I. Deqian, 2017)	1.000	-6.40(L. I. Deqian, 2017)	-6.57	0.17
14	Yb	$logD = 2.90pH - 5.750$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 5.84$(L. I. Deqian, 2017)	0.998	-5.84(L. I. Deqian, 2017)	-6.22	0.38
15	Lu	$logD = 2.85pH - 5.550$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 5.80$(L. I. Deqian, 2017)	0.997	-5.80(L. I. Deqian, 2017)	-5.87	0.07
16	Y	$logD = 2.95pH - 6.775$(L. I. Deqian, 2017)	1.000	$logD = 3pH - 6.50$(L. I. Deqian, 2017)		-6.55(L. I. Deqian, 2017)	-7.12	

Table A.10- Part A Relation between log D and pH for D2EHEPA

Solvent Extractant		**D2EHEPA**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.40	0.38
1	La	$logD = 2.7672pH - 3.7314$(Chen et al., 2020)	0.995	$logD = 3pH -$ 4.08(Chen et al., 2020)	0.993	-4.08(Chen et al., 2020)	-4.05	0.03
2	Ce	$logD = 2.8236pH - 3.2956$(Chen et al., 2020)	0.989	$logD = 3pH -$ 3.75(Chen et al., 2020)	0.996	-3.75(Chen et al., 2020)	-3.70	0.05
3	Pr	$logD = 2.7473pH - 2.6081$(Chen et al., 2020)	0.963	$logD = 3pH -$ 3.15(Chen et al., 2020)	0.993	-3.15(Chen et al., 2020)	-3.35	0.20
4	Nd	$logD = 2.8459pH - 1.2367$(Chen et al., 2020)	0.904	$logD = 3pH -$ 1.78(Chen et al., 2020)	0.994	-1.78(Chen et al., 2020)	-3.01	1.23
5	Pm						-2.66	
6	Sm						-2.31	
7	Eu						-1.96	
8	Gd						-1.61	

Table A.10- Part B Relation between log D and pH for D2EHEPA

Solvent Extractant		**D2EHEPA**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.40	0.38
9	Tb						-1.26	
10	Dy						-0.92	
11	Ho						-0.57	
12	Er						-0.22	
13	Tm						0.13	
14	Yb						0.48	
15	Lu						0.83	
16	Y						-0.42	

Table A.11-Part A Relation between log D and pH for DNPP at 0.2 M Concentration

Solvent Extractant		**DNPP**		**Concentration**		**0.2 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							0.50	0.47
1	La	$logD = -3.11pH +$ 1.18(Anitha et al., 2014)	0.995	$logD = -3pH +$ 1(Anitha et al., 2014)	0.999	1.00(Anitha et al., 2014)	0.85	0.15
2	Ce						1.20	
3	Pr						1.55	
4	Nd						1.89	
5	Pm						2.24	
6	Sm						2.59	
7	Eu						2.94	
8	Gd						3.29	

Table A.11-Part B Relation between log D and pH for DNPP at 0.2 M Concentration

Solvent Extractant		**DNPP**		**Concentration**		**0.2 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							0.50	0.47
9	Tb						3.64	
10	Dy	$logD = -2.9pH -$ 2.79(Anitha et al., 2014)	0.995	$logD = -3pH +$ 3(Anitha et al., 2014)	0.999	3.00(Anitha et al., 2014)	3.98	0.98
11	Ho						4.33	
12	Er						4.68	
13	Tm						5.03	
14	Yb						5.38	
15	Lu						5.73	
16	Y	$logD = -3.03pH +$ 4.2(Anitha et al., 2014)	0.995	$logD = -3pH +$ 4.1(Anitha et al., 2014)	0.999	4.20(Anitha et al., 2014)	4.48	0.28

Table A.12-Part A Relation between log D and pH for Cyanex 572

Solvent Extractant		**Cyanex 572**		**Concentration**	**N/A**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-5.40	0.62
1	La						-5.05	
2	Ce						-4.70	
3	Pr						-4.35	
4	Nd						-4.01	
5	Pm						-3.66	
6	Sm						-3.31	
7	Eu						-2.96	
8	Gd						-2.61	

Table A.12-Part B Relation between log D and pH for Cyanex 572

Solvent Extractant		**Cyanex 572**		**Concentration**	**N/A**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-5.40	0.62
9	Tb						-2.26	
10	Dy						-1.92	
11	Ho	$logD = 2.92pH - 1.1000$(Y. Wang et al., 2015)		$logD = 3pH - 1.3$(Y. Wang et al., 2015)	0.999	-1.30(Y. Wang et al., 2015)	-1.57	0.27
12	Er	$logD = 2.90pH - 0.3750$(Y. Wang et al., 2015)		$logD = 3pH - 0.6$ (Y. Wang et al., 2015)	0.999	-0.60(Y. Wang et al., 2015)	-1.22	0.62
13	Tm	$logD = 2.95pH - 0.5625$(Y. Wang et al., 2015)		$logD = 3pH - 0.6$ (Y. Wang et al., 2015)	1.000	-0.60(Y. Wang et al., 2015)	-0.87	0.27
14	Yb	$logD = 2.57pH - 0.4625$(Y. Wang et al., 2015)		$logD = 3pH - 1.4$ (Y. Wang et al., 2015)	0.979	-1.40(Y. Wang et al., 2015)	-0.52	0.88
15	Lu	$logD = 3.41pH - 0.0250$(Y. Wang et al., 2015)		$logD = 3pH + 0.9$ (Y. Wang et al., 2015)	0.981	0.900(Y. Wang et al., 2015)	-0.17	1.07
16	Y						-1.42	

Table A.13- Part A Relation between log D and pH for HEHEMP at 0.1 M Concentration

Solvent Extractant		**HEHEMP**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-6.80	0.09
1	La						-6.45	
2	Ce						-6.10	
3	Pr						-5.75	
4	Nd						-5.41	
5	Pm						-5.06	
6	Sm						-4.71	
7	Eu						-4.36	
8	Gd						-4.01	

Table A.13- Part B Relation between log D and pH for HEHEMP at 0.1 M Concentration

Solvent Extractant		**HEHEMP**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-6.80	0.09
9	Tb						-3.66	
10	Dy						-3.32	
11	Ho	$logD = 2.7875pH - 2.4663$ (Q. Zhao et al., 2019)	0.999	$logD = 3pH - 2.90$ (Q. Zhao et al., 2019)	0.994	-2.90 (Q. Zhao et al., 2019)	-2.97	0.07
12	Er	$logD = 2.7675pH - 2.1243$ (Q. Zhao et al., 2019)	0.999	$logD = 3pH - 2.58$ (Q. Zhao et al., 2019)	0.994	-2.58 (Q. Zhao et al., 2019)	-2.62	0.04
13	Tm	$logD = 2.9125pH - 1.8913$ (Q. Zhao et al., 2019)	0.999	$logD = 3pH - 2.08$ (Q. Zhao et al., 2019)	0.999	-2.08 (Q. Zhao et al., 2019)	-2.27	0.19
14	Yb	$logD = 2.8675pH - 1.6643$ (Q. Zhao et al., 2019)	0.999	$logD = 3pH - 1.93$ (Q. Zhao et al., 2019)	0.998	-1.93 (Q. Zhao et al., 2019)	-1.92	0.01
15	Lu	$logD = 2.9275pH - 1.5178$ (Q. Zhao et al., 2019)	1.000	$logD = 3pH - 1.57$ (Q. Zhao et al., 2019)	0.999	-1.57 (Q. Zhao et al., 2019)	-1.57	0.00
16	Y	$logD = 2.7375pH - 2.0863$ (Q. Zhao et al., 2019)	0.999	$logD = 3pH - 2.62$ (Q. Zhao et al., 2019)	0.991	-2.62 (Q. Zhao et al., 2019)	-2.82	0.20

Table A.14-Part A Relation between log D and pH for HL4 at 0.002 M Concentration

Solvent Extractant		**HL4**		**Concentration**	**0.002 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.20	0.36
1	La	$logD = -3.012pH - 2.8500$ (Y. Lu & Liao, 2016)		$logD = -3pH - 2.9$ (Y. Lu & Liao, 2016)	1.000	-2.90 (Y. Lu & Liao, 2016)	-3.85	0.95
2	Ce						-3.50	
3	Pr	$logD = -3.075pH - 2.2500$ (Y. Lu & Liao, 2016)		$logD = -3pH - 2.4$ (Y. Lu & Liao, 2016)	0.999	-2.40 (Y. Lu & Liao, 2016)	-3.15	0.75
4	Nd						-2.81	
5	Pm						-2.46	
6	Sm						-2.11	
7	Eu						-1.76	
8	Gd	$logD = -3.100pH - 1.1800$ (Y. Lu & Liao, 2016)		$logD = -3pH - 1.4$ (Y. Lu & Liao, 2016)	0.999	-1.39 (Y. Lu & Liao, 2016)	-1.41	0.02

Table A.14-Part B Relation between log D and pH for HL4 at 0.002 M Concentration

Solvent Extractant		**HL4**		**Concentration**	**0.002 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.20	0.36
9	Tb	$logD = -3.100pH - 0.6350$ (Y. Lu & Liao, 2016)		$logD = -3pH - 0.8$ (Y. Lu & Liao, 2016)	0.999	-0.83 (Y. Lu & Liao, 2016)	-1.06	0.23
10	Dy						-0.72	
11	Ho						-0.37	
12	Er						-0.02	
13	Tm						0.33	
14	Yb	$logD = -3.000pH + 0.5833$ (Y. Lu & Liao, 2016)		$logD = -3pH + 0.6$ (Y. Lu & Liao, 2016)	1.000	0.58 (Y. Lu & Liao, 2016)	0.68	0.09
15	Lu	$logD = -3.000pH + 0.9330$ (Y. Lu & Liao, 2016)		$logD = -3pH + 0.9$ (Y. Lu & Liao, 2016)	1.000	0.93 (Y. Lu & Liao, 2016)	1.03	0.09
16	Y						-0.22	

Table A.15-Part A Relation between log D and pH for HEHAPP at 0.05 M concentration

Solvent Extractant		**HEHAPP**		**Concentration**	**0.05 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.10	0.76
1	La	$logD = -2.8533pH - 1.7840$ (Kuang et al., 2018)	0.999	$logD = 3pH - 1.5$ (Kuang et al., 2018)	0.998	-1.50 (Kuang et al., 2018)	-3.75	2.25
2	Ce						-3.40	
3	Pr						-3.05	
4	Nd						-2.71	
5	Pm						-2.36	
6	Sm						-2.01	
7	Eu						-1.66	
8	Gd	$logD = -2.9667pH - 1.1650$ (Kuang et al., 2018)	0.999	$logD = 3pH - 1.1$ (Kuang et al., 2018)	1.000	-1.10 (Kuang et al., 2018)	-1.31	0.21

Table A.15-Part B Relation between log D and pH for HEHAPP at 0.05 M concentration

Solvent Extractant		**HEHAPP**		**Concentration**	**0.05 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-4.10	0.76
9	Tb						-0.96	
10	Dy						-0.62	
11	Ho						-0.27	
12	Er						0.08	
13	Tm						0.43	
14	Yb						0.78	
15	Lu	$logD = -3.2330pH + 1.9033$ (Kuang et al., 2018)	0.999	$logD = 3pH + 1.4$ (Kuang et al., 2018)	0.994	1.40 (Kuang et al., 2018)	1.13	0.27
16	Y	$logD = -3.1667pH - 0.5333$ (Kuang et al., 2018)	0.994	$logD = 3pH + 0.18$ (Kuang et al., 2018)	0.997	0.18 (Kuang et al., 2018)	-0.12	0.30

Table A.16- Part A Relation between log D and pH for Cekaonic Acid at 0.56 M Concentration

Solvent Extractant		**Cekaonic Acid**		**Concentration**	**0.56 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-14.60	1.09
1	La	$logD = 3.06pH - 13.85$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.76$ (Singh et al., 2006)	0.999	-13.76 (Singh et al., 2006)	-14.25	0.49
2	Ce	$logD = 3.03pH - 13.24$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.18$ (Singh et al., 2006)	0.999	-13.18 (Singh et al., 2006)	-13.90	0.72
3	Pr	$logD = 3.12pH - 13.64$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.36$ (Singh et al., 2006)	0.998	-13.36 (Singh et al., 2006)	-13.55	0.19
4	Nd	$logD = 3.07pH - 13.25$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.12$ (Singh et al., 2006)	0.999	-13.12 (Singh et al., 2006)	-13.21	0.09
5	Pm						-12.86	
6	Sm	$logD = 3.06pH - 13.11$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.09$ (Singh et al., 2006)	0.999	-13.09 (Singh et al., 2006)	-12.51	0.58
7	Eu						-12.16	
8	Gd	$logD = 3.11pH - 13.16$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.02$ (Singh et al., 2006)	0.998	-13.02 (Singh et al., 2006)	-11.81	1.21

Table A.16- Part B Relation between log D and pH for Cekaonic Acid at 0.56 M Concentration

Solvent Extractant		**Cekaonic Acid**		**Concentration**	**0.56 M**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-14.60	1.09
9	Tb						-11.46	
10	Dy	$logD = 2.74pH - 11.55$ (Singh et al., 2006)	1.000	$logD = 3pH - 12.02$ (Singh et al., 2006)	0.992	-12.02 (Singh et al., 2006)	-11.12	0.98
11	Ho	$logD = 3.35pH - 14.00$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.35$ (Singh et al., 2006)	0.986	-13.35 (Singh et al., 2006)	-10.77	2.58
12	Er						-10.42	
13	Tm						-10.07	
14	Yb						-9.72	
15	Lu						-9.37	
16	Y	$logD = 3.14pH - 13.78$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.55$ (Singh et al., 2006)	0.998	-13.55 (Singh et al., 2006)	-10.62	2.93

Table A.17-Part A Relation between log D and pH for Neo Heptanic Acid at 0.73 M Concentration

Solvent Extractant		**Neo Heptanic Acid**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-15.10	1.49
1	La	$logD = 2.73pH - 13.89$ (Singh et al., 2006)	1.000	$logD = 3pH - 14.60$ (Singh et al., 2006)	0.999	-14.60 (Singh et al., 2006)	-14.75	0.15
2	Ce						-14.40	
3	Pr	$logD = 3.07pH - 15.09$ (Singh et al., 2006)	1.000	$logD = 3pH - 15.04$ (Singh et al., 2006)	0.998	-15.04 (Singh et al., 2006)	-14.05	0.99
4	Nd	$logD = 2.86pH - 13.91$ (Singh et al., 2006)	1.000	$logD = 3pH - 14.15$ (Singh et al., 2006)	0.999	-14.15 (Singh et al., 2006)	-13.71	0.44
5	Pm						-13.36	
6	Sm	$logD = 2.95pH - 14.01$ (Singh et al., 2006)	1.000	$logD = 3pH - 14.05$ (Singh et al., 2006)	0.999	-14.05 (Singh et al., 2006)	-13.01	1.04
7	Eu						-12.66	
8	Gd	$logD = 3.32pH - 15.42$ (Singh et al., 2006)	1.000	$logD = 3pH - 15.01$ (Singh et al., 2006)	0.998	-15.01 (Singh et al., 2006)	-12.31	2.70

Table A.17-Part B Relation between log D and pH for Neo Heptanic Acid at 0.73 M Concentration

Solvent Extractant		**Neo Heptanic Acid**		**Concentration**		**0.73 M**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-15.10	1.49
9	Tb						-11.96	
10	Dy	$logD = 3.15pH - 14.43$ (Singh et al., 2006)	1.000	$logD = 3pH - 14.10$ (Singh et al., 2006)	0.992	-14.10 (Singh et al., 2006)	-11.62	2.48
11	Ho	$logD = 2.90pH - 13.14$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.30$ (Singh et al., 2006)	0.986	-13.30 (Singh et al., 2006)	-11.27	2.03
12	Er						-10.92	
13	Tm						-10.57	
14	Yb						-10.22	
15	Lu						-9.87	
16	Y	$logD = 2.81pH - 12.97$ (Singh et al., 2006)	1.000	$logD = 3pH - 13.20$ (Singh et al., 2006)	0.995	-13.20 (Singh et al., 2006)	-11.12	2.08

Table A.18-Part A Relation between log D and pH for Cyanex 301 at 0.2 M Concentration and Cyanex 923 at 0.01 M Concentration

Solvent Extractant		**Cyanex 301 + Cyanex 923**		**Concentration**		**Cyanex 301(0.2 M) +Cyanex 923 (0.01 M)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							<u>-6.80</u>	<u>0.28</u>
1	La	$logD = -3.0625pH - 6.2125$ (M. L. P. Reddy et al., 1999)	0.998	$logD = -3pH - 6.35$ (M. L. P. Reddy et al., 1999)	1.000	-6.35(M. L. P. Reddy et al., 1999)	-6.45	0.10
2	Ce						-6.10	
3	Pr						-5.75	
4	Nd	$logD = -3.0625pH - 5.6958$ (M. L. P. Reddy et al., 1999)	0.999	$logD = -3pH - 5.80$ (M. L. P. Reddy et al., 1999)	1.000	-5.80 (M. L. P. Reddy et al., 1999)	-5.41	0.39
5	Pm						-5.06	
6	Sm						-4.71	
7	Eu	$logD = -3.0000pH - 4.7167$ (M. L. P. Reddy et al., 1999)	0.999	$logD = -3pH - 4.72$ (M. L. P. Reddy et al., 1999)	1.000	-4.72 (M. L. P. Reddy et al., 1999)	-4.36	0.36
8	Gd						-4.01	

Table A.18-Part B Relation between log D and pH for Cyanex 301 at 0.2 M Concentration and Cyanex 923 at 0.01 M Concentration

Solvent Extractant		**Cyanex 301 + Cyanex 923**		**Concentration**		**Cyanex 301 (0.2 M) +Cyanex 923 (0.01 M)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-6.80	0.28
9	Tb	$logD = -3.0625pH - 3.3958$ (M. L. P. Reddy et al., 1999)	1.000	$logD = -3pH - 3.50$ (M. L. P. Reddy et al., 1999)	1.000	-3.50 (M. L. P. Reddy et al., 1999)	-3.66	0.16
10	Dy						-3.32	
11	Ho	$logD = -3.0000pH - 2.5500$ (M. L. P. Reddy et al., 1999)	1.000	$logD = -3pH - 2.55$ (M. L. P. Reddy et al., 1999)	1.000	-2.55 (M. L. P. Reddy et al., 1999)	-2.97	0.42
12	Er						-2.62	
13	Tm	$logD = -3.0000pH - 1.8500$ (M. L. P. Reddy et al., 1999)	1.000	$logD = -3pH - 1.85$ (M. L. P. Reddy et al., 1999)	1.000	-1.85 (M. L. P. Reddy et al., 1999)	-2.27	0.42
14	Yb						-1.92	
15	Lu	$logD = -3.0000pH - 1.4500$ (M. L. P. Reddy et al., 1999)	1.000	$logD = -3pH - 1.45$ (M. L. P. Reddy et al., 1999)	1.000	-1.45 (M. L. P. Reddy et al., 1999)	-1.57	0.12
16	Y	$logD = -3.0625pH - 2.4458$ (M. L. P. Reddy et al., 1999)	0.999	$logD = -3pH - 2.60$ (M. L. P. Reddy et al., 1999)	1.000	-2.60 (M. L. P. Reddy et al., 1999)	-2.82	0.22

Table A.19-Part A Relation between log D and pH for HEDHP at 0.04 M Concentration and HEH/EHP at 0.06 M Concentration

Solvent Extractant		**HEDHP and HEH/EHP**		**Concentration**		**HEDHP (0.04 M) + HEH/EHP (0.06 M)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-6.40	0.37
1	La	$logD = 2.900pH - 6.220$ (Zhang et al., 2008)	0.996	$logD = 3pH - 6.5$ (Zhang et al., 2008)	0.999	-6.50 (Zhang et al., 2008)	-6.05	0.45
2	Ce						-5.70	
3	Pr						-5.35	
4	Nd	$logD = 2.950pH - 4.605$ (Zhang et al., 2008)	0.999	$logD = 3pH - 4.7$ (Zhang et al., 2008)	1.000	-4.70 (Zhang et al., 2008)	-5.01	0.31
5	Pm						-4.66	
6	Sm	$logD = 2.850pH - 3.600$ (Zhang et al., 2008)	0.999	$logD = 3pH - 3.9$ (Zhang et al., 2008)	0.998	-3.90 (Zhang et al., 2008)	-4.31	0.41
7	Eu						-3.96	
8	Gd	$logD = 2.625pH - 2.725$ (Zhang et al., 2008)	0.999	$logD = 3pH - 3.3$ (Zhang et al., 2008)	0.983	-3.30 (Zhang et al., 2008)	-3.61	0.31

Table A.19-Part B Relation between log D and pH for HEDHP at 0.04 M Concentration and HEH/EHP at 0.06 M Concentration

Solvent Extractant		**HEDHP and HEH/EHP**		**Concentration**		**HEDHP (0.04 M) + HEH/EHP (0.06 M)**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-6.40	0.37
9	Tb						-3.26	
10	Dy						-2.92	
11	Ho						-2.57	
12	Er						-2.22	
13	Tm						-1.87	
14	Yb						-1.52	
15	Lu						-1.17	
16	Y						-2.42	

Table A.20-Part A Relation between log D and pH for EHEHPA

Solvent Extractant		**EHEHPA**		**Concentration**		**N/A**		
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-7.20	0.27
1	La						-6.85	
2	Ce						-6.50	
3	Pr	$logD = 3.050pH - 6.1667$ (Registered et al., 2007)	0.999	$logD = 3pH - 6.07$ (Registered et al., 2007)	1.000	-6.07 (Registered et al., 2007)	-6.15	0.08
4	Nd	$logD = 3.025pH - 5.9667$ (Registered et al., 2007)	1.000	$logD = 3pH - 5.92$ (Registered et al., 2007)	1.000	-5.92 (Registered et al., 2007)	-5.81	0.11
5	Pm						-5.46	
6	Sm	$logD = 3.040pH - 4.9200$ (Registered et al., 2007)	0.999	$logD = 3pH - 4.86$ (Registered et al., 2007)	1.000	-4.86 (Registered et al., 2007)	-5.11	0.25
7	Eu	$logD = 3.010pH - 4.5050$ (Registered et al., 2007)	0.999	$logD = 3pH - 4.50$ (Registered et al., 2007)	1.000	-4.50 (Registered et al., 2007)	-4.76	0.26
8	Gd	$logD = 3.060pH - 4.3750$ (Registered et al., 2007)	1.000	$logD = 3pH - 4.24$ (Registered et al., 2007)	1.000	-4.24 (Registered et al., 2007)	-4.41	0.17

Table A.20-Part B Relation between log D and pH for EHEHPA

Solvent Extractant		**EHEHPA**		**Concentration**	**N/A**			
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-7.20	0.27
9	Tb						-4.06	
10	Dy						-3.72	
11	Ho	$logD = 3.060pH - 3.0200$ (Registered et al., 2007)	0.999	$logD = 3pH - 2.94$ (Registered et al., 2007)	1.000	-2.94 (Registered et al., 2007)	-3.37	0.43
12	Er	$logD = 3.020pH - 2.6400$ (Registered et al., 2007)	0.999	$logD = 3pH - 2.62$ (Registered et al., 2007)	1.000	-2.62 (Registered et al., 2007)	-3.02	0.40
13	Tm						-2.67	
14	Yb						-2.32	
15	Lu						-1.97	
16	Y	$logD = 3.000pH - 2.7500$ (Registered et al., 2007)	0.999	$logD = 3pH - 2.75$ (Registered et al., 2007)	1.000	-2.75 (Registered et al., 2007)	-3.22	0.47

Table A.21-Part A Relation between log D and pH for P227 at 0.16 M Concentration

Solvent Extractant		**P227**		**Concentration**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**MAE**
							-7.33	0.07
1	La						-6.98	
2	Ce						-6.63	
3	Pr						-6.28	
4	Nd						-5.94	
5	Pm						-5.59	
6	Sm						-5.24	
7	Eu						-4.89	
8	Gd						-4.54	

Table A.21-Part B Relation between log D and pH for P227 at 0.16 M Concentration

Solvent Extractant		**P227**		**Concentration**		**0.16 M**				
No	**REE**	**log D vs pH (Experimental)**	**R^2**	**log D vs pH (Curve Fitting)**		**R^2**	**Model 1**			
							Intercept	**Model**	**MAE**	
								-7.33	0.07	
9	Tb							-4.19		
10	Dy							-3.85		
11	Ho	$logD = 2.7650pH - 3.0120$ (Chen et al., 2020)	0.999	$logD = 3pH - 3.50$	(Chen et al., 2020)	0.994	-3.50 (Chen et al., 2020)	-3.50	0.00	
12	Er	$logD = 2.7500pH - 2.7250$ (Chen et al., 2020)	1.000	$logD = 3pH - 3.21$	(Chen et al., 2020)	0.994	-3.21 (Chen et al., 2020)	-3.15	0.06	
13	Tm	$logD = 2.7500pH - 2.3500$ (Chen et al., 2020)	1.000	$logD = 3pH - 2.86$	(Chen et al., 2020)	0.999	-2.86 (Chen et al., 2020)	-2.80	0.06	
14	Yb	$logD = 2.9125pH - 2.1900$ (Chen et al., 2020)	0.999	$logD = 3pH - 2.36$	(Chen et al., 2020)	0.998	-2.36 (Chen et al., 2020)	-2.45	0.09	
15	Lu	$logD = 3.0875pH - 2.0850$ (Chen et al., 2020)	0.999	$logD = 3pH - 1.92$	(Chen et al., 2020)	0.999	-1.92 (Chen et al., 2020)	-2.10	0.18	
16	Y	$logD = 2.6625pH - 2.7175$ (Chen et al., 2020)	0.999	$logD = 3pH - 3.38$	(Chen et al., 2020)	0.987	-3.38 (Chen et al., 2020)	-3.35	0.03	

APPENDIX B

Table B.1-Part A- log D and pH calculations for Cyanex 272 at 1 M concentration

Extractant		**Cyanex 272 (Quinn et al., 2015)**					**Concentration**		**1 M**				
REE	**pH**	**Log D_{Ex}**	**Log D_{Nu}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log D_{Nu}**	**Log $D_{G=3}$**		
Ce	1.5	-2.0	-1.9	-1.9	3.6	0.006	Pr	1.5	-1.7	-1.6	-1.7	2.7	0.000
	1.8	-0.9	-1.0	-1.0	1.0	0.014		1.8	-0.5	-0.7	-0.8	0.5	0.078
	2.0	-0.5	-0.4	-0.4	0.2	0.006		2.0	-0.2	-0.1	-0.2	0.0	0.000
	2.3	0.4	0.5	0.5	0.2	0.006		2.3	0.7	0.8	0.7	0.6	0.000
	2.6	1.2	1.2	1.2	1.6	0.001		2.6	1.5	1.5	1.5	2.3	0.001
	2.7	1.7	1.7	1.7	2.9	0.000							
		0.0	-6.5	-6.4	9.5	0.035			0.0	-6.0	-6.2	6.1	0.080
R^2						0.996	R^2						0.987
Nd	1.5	-1.6	-1.5	-1.5	2.6	0.010	Sm	1.0	-1.9	-2.0	-1.8	3.2	0.010
	1.8	-0.4	-0.6	-0.6	0.5	0.040		1.3	-1.4	-1.2	-1.1	1.1	0.123
	2	0.0	0.0	0.0	0.0	0.000		1.5	-0.3	-0.4	-0.3	0.1	0.000
	2.3	0.9	0.9	0.9	0.6	0.000		1.8	0.6	0.4	0.5	0.2	0.022
	2.6	1.7	1.7	1.7	2.3	0.003		2.0	1.1	1.2	1.2	1.4	0.010
								2.3	1.9	2.0	2.0	3.8	0.003
		0.1	-6.1	-6.0	6.1	0.052			0.0	-5.1	-4.8	9.9	0.168
R^2						0.991	R^2						0.983
Tb	1.0	-1.6	-1.6	-1.6	0.1	0.000	Dy	1.0	-1.2	-1.2	-1.3	0.1	0.003
	1.1	-1.3	-1.3	-1.3	0.0	0.000		1.1	-0.9	-0.9	-0.9	0.0	0.002
	1.2	-0.9	-0.9	-0.9	0.1	0.001		1.2	-0.5	-0.5	-0.5	0.1	0.001
		-1.3	-4.6	-4.5	0.3	0.001			-0.9	-4.0	-4.1	0.3	0.006
						0.997							0.978

Table B.1-Part B- log D and pH calculations for Cyanex 272 at 1 M concentration

Extractant		**Cyanex 272 (Quinn et al., 2015)**					**Concentration**		**1 M**				
REE	**pH**	**Log D_{Ex}**	**Log D_{Nu}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log D_{Nu}**	**Log $D_{G=3}$**		
Ho	1.0	-1.0	-0.9	-1.0	0.1	0.000	Er	0.6	-1.6	-1.6	-1.6	1.1	0.001
	1.1	-0.6	-0.6	-0.6	0.0	0.002		1.0	-0.6	-0.5	-0.6	0.0	0.002
	1.2	-0.2	-0.1	-0.2	0.1	0.006		1.1	-0.3	-0.2	-0.3	0.1	0.000
								1.2	0.2	0.2	0.2	0.5	0.001
		-0.6	-4.1	-3.8	0.3	0.009			-0.6	-3.4	-3.4	1.2	0.003
R^2						0.967	R^2						0.997
Yb	0.1	-1.8	-1.9	-1.9	2.9	0.020	Lu	0.1	-1.6	-1.6	-1.8	3.0	0.026
	0.3	-1.4	-1.4	-1.4	1.4	0.001		0.3	-1.2	-1.2	-1.3	1.5	0.010
	0.6	-0.6	-0.5	-0.5	0.1	0.005		0.6	-0.4	-0.3	-0.4	0.1	0.000
	1.0	0.5	0.5	0.6	0.6	0.010		1.0	0.6	0.6	0.7	0.6	0.017
	1.1	0.8	0.8	0.9	1.2	0.010		1.1	1.0	0.9	1.0	1.1	0.006
	1.2	1.2	1.1	1.3	2.3	0.005		1.2	1.3	1.3	1.5	2.2	0.022
		-0.2	-2.2	-2.3	8.5	0.050			0.0	-1.9	-2.1	8.5	0.081
R^2						0.994	R^2						0.990
Y	0.6	-1.8	-1.8	-1.8	1.2	0.001							
	1.0	-0.8	-0.7	-0.8	0.0	0.000							
	1.1	-0.5	-0.4	-0.5	0.1	0.000							
	1.2	0.0	0.0	0.0	0.5	0.001							
R^2		-0.8	-3.6	-3.6	1.3	0.001							

Table B.2- log D and pH calculations for Cyanex 572 at 1 M concentration

Extractant		**Cyanex 572 (Quinn et al., 2015)**			**Concentration**		**1 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ce	0.0	-4.5	-4.5	36.1	0.002	Pr	0.0	-4.2	-4.2	36.7	0.002
	1.0	-1.5	-1.5	9.0	0.000		1.0	-1.2	-1.2	9.4	0.000
	2.0	1.5	1.5	0.0	0.000		2.0	1.9	1.8	0.0	0.003
	3.0	4.5	4.5	9.0	0.001		3.0	4.9	4.8	8.7	0.012
	4.0	7.6	7.5	35.9	0.003		4.0	8.0	7.8	35.3	0.025
R^2		1.5	-4.5	90.0	0.006	R^2		1.9	-4.2	90.0	0.042
					1.000						1.000
Nd	0.0	-4.1	-4.0	35.9	0.011	Sm	0.0	-3.3	-2.7	36.0	0.360
	1.0	-1.0	-1.0	9.0	0.003		1.0	0.0	0.4	9.0	0.090
	2.0	2.0	2.0	0.0	0.000		2.0	3.4	3.4	0.0	0.000
	3.0	5.1	5.0	9.0	0.002		3.0	6.7	6.4	9.0	0.090
	4.0	8.1	8.0	36.1	0.009		4.0	10.0	9.4	36.0	0.360
R^2		2.0	-4.0	90.0	0.025	R^2		3.4	-2.7	90.0	0.900
					1.000						0.990

Table B.3 -Part A- log D and pH calculations for D2EHEPA at 1.56 M concentration

Extractant		**D2EHEPA (Ohto et al., 1995)**				**Concentration**		**1.56 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-4.2	-4.2	36.0	0.000	Ce	0.0	-3.1	-3.1	23	0.000
	1.0	-1.2	-1.2	9.0	0.000		1.2	0.5	0.5	1	0.000
	2.0	1.8	1.8	0.0	0.000		3.0	5.9	5.9	18	0.000
	3.0	4.8	4.8	9.0	0.000		4.0	8.9	8.9	52	0.000
	4.0	7.8	7.8	36.0	0.000						
R^2		1.8	-4.2	90.0	0.000	R^2		1.7	-3.1	122	0.000
					1.000						1.000
Pr	0.0	-3.7	-3.7	36.6	0.000	Nd	0.0	-3.4	-3.3	32.9	0.025
	1.0	-0.7	-0.7	9.3	0.001		1.0	-0.5	-0.3	7.5	0.044
	2.0	2.3	2.3	0.0	0.002		2.0	2.5	2.8	0.1	0.068
	3.0	5.4	5.3	8.7	0.006		3.0	5.4	5.8	10.6	0.098
	4.0	8.4	8.3	35.4	0.010		4.0	8.4	8.8	39.2	0.132
R^2		2.3	-3.7	90.0	0.019	R^2		2.5	-3.3	90.3	0.367
					1.000						0.996
Sm	0.0	-2.9	-3.3	39.5	0.117	Gd	0.0	-2.6	-2.7	36.1	0.019
	1.0	0.0	-0.3	10.8	0.099		1.0	0.4	0.3	9.0	0.005
	2.0	3.0	2.7	0.1	0.082		2.0	3.3	3.3	0.0	0.000
	3.0	6.0	5.7	7.4	0.067		3.0	6.2	6.3	9.0	0.004
	4.0	9.0	8.7	32.6	0.054		4.0	9.2	9.3	35.9	0.016
R^2		3.0	-3.3	90.4	0.419	R^2		3.3	-2.7	90.0	0.044

Table B.3 -Part B- log D and pH calculations for D2EHEPA at 1.56 M concentration

Extractant		**D2EHEPA (Ohto et al., 1995)**			**Concentration**		**1.56 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ho	0.0	-0.8	-0.8	36.0	0.000	Er	0.0	-0.4	-0.4	36.1	0.000
	1.0	2.2	2.2	9.0	0.000		1.0	2.6	2.6	9.0	0.000
	2.0	5.2	5.2	0.0	0.000		2.0	5.6	5.6	0.0	0.000
	3.0	8.2	8.2	9.0	0.000		3.0	8.6	8.6	9.0	0.000
	4.0	11.2	11.2	36.0	0.000		4.0	11.6	11.6	35.9	0.000
R^2		5.2	-0.8	90.0	0.000	R^2		5.6	-0.4	90.0	0.000

Table B.4 -Part A- log D and pH calculations for EHEHPA at 1.61 M Concentration

Extractant		**EHEHPA (Ohto et al., 1995)**			**Concentration**		**1.61 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-4.3	-4.2	34.4	0.017	Ce	0.0	-3.8	-3.8	35.2	0.000
	1.0	-1.3	-1.2	8.2	0.017		1.0	-0.8	-0.8	8.6	0.001
	2.0	1.7	1.8	0.0	0.017		2.0	2.1	2.2	0.0	0.004
	3.0	4.7	4.8	9.8	0.018		3.0	5.1	5.2	9.4	0.011
	4.0	7.7	7.8	37.6	0.018		4.0	8.1	8.2	36.8	0.021
R^2		1.7	-4.2	90.1	0.086	R^2		2.1	-3.8	90.0	0.038
					0.999						1.000

Table B.4-Part B- log D and pH calculations for EHEHPA at 1.61 M concentration

Extractant	**EHEHPA (Ohto et al., 1995)**					**Concentration**				**1.61 M**
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Pr	0.0	-3.7	-3.7	36.2	0.000	Nd	0.0	-3.5	-3.5	36.0	0.000
	1.0	-0.7	-0.7	9.1	0.000		1.0	-0.5	-0.5	9.0	0.000
	2.0	2.3	2.3	0.0	0.000		2.0	2.5	2.5	0.0	0.000
	3.0	5.3	5.3	8.9	0.000		3.0	5.5	5.5	9.0	0.000
	4.0	8.3	8.3	35.8	0.000		4.0	8.5	8.5	36.0	0.000
R^2		2.3	-3.7	90.0	0.002	R^2		2.5	-3.5	90.0	0.000
					1.000						1.000
Sm	0.0	-2.8	-2.8	34.9	0.000	Gd	0.0	-2.3	-2.3	35.2	0.000
	1.0	0.1	0.2	8.4	0.003		1.0	0.7	0.7	8.6	0.001
	2.0	3.1	3.2	0.0	0.009		2.0	3.6	3.7	0.0	0.004
	3.0	6.0	6.2	9.6	0.019		3.0	6.6	6.7	9.4	0.011
	4.0	9.0	9.2	37.1	0.033		4.0	9.6	9.7	36.8	0.019
R^2		3.1	-2.8	90.0	0.063	R^2		3.6	-2.3	90.0	0.036
					0.999						1.000
Ho	0.0	-0.8	-0.8	36.0	0.000	Er	0.0	-0.4	-0.4	36.1	0.000
	1.0	2.2	2.2	9.0	0.000		1.0	2.6	2.6	9.0	0.000
	2.0	5.2	5.2	0.0	0.000		2.0	5.6	5.6	0.0	0.000
	3.0	8.2	8.2	9.0	0.000		3.0	8.6	8.6	9.0	0.000
	4.0	11.2	11.2	36.0	0.000		4.0	11.6	11.6	35.9	0.000
R^2		5.2	-0.8	90.0	0.000	R^2		5.6	-0.4	90.0	0.000
					1.000						1.000

Table B.5- log D and pH calculations for EHEPA at 1 M concentration

Extractant	**EHEPA (Quinn et al., 2015)**		**Concentration**			**1 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ce	0.0	-3.8	-3.5	36.8	0.151	Pr	0.0	-3.5	-3.1	36.1	0.143
	1.0	-0.6	-0.5	9.4	0.027		1.0	-0.3	-0.1	9.0	0.035
	2.0	2.6	2.6	0.0	0.004		2.0	2.9	2.9	0.0	0.000
	3.0	5.8	5.6	8.6	0.083		3.0	6.1	5.9	9.0	0.038
	4.0	9.1	8.6	35.2	0.265		4.0	9.3	8.9	35.9	0.150
R^2		2.6	-3.5	90.0	0.530	R^2		2.9	-3.1	90.0	0.366
					0.994						0.996
Nd	0.0	-3.4	-2.8	33.4	0.346	Sm	0.0	-2.5	-2.4	39.1	0.017
	1.0	-0.2	0.2	7.7	0.165		1.0	0.7	0.6	10.6	0.004
	2.0	3.0	3.2	0.1	0.050		2.0	3.9	3.6	0.1	0.063
	3.0	6.2	6.2	10.4	0.002		3.0	7.1	6.6	7.6	0.196
	4.0	9.4	9.2	38.7	0.019		4.0	10.2	9.6	33.0	0.402
R^2		3.0	-2.8	90.3	0.583	R^2		3.9	-2.4	90.3	0.683
					0.994						0.992

Table B.6- log D and pH calculations for Cyanex 272 at 0.1 M concentration

Extractant	**Cyanex 272 (Komatsu & Freiser, 1989)**				**Concentration**	**0.1 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-13.1	-12.4	35.2	0.423	Pr	0.0	-9.3	-9.6	34.6	0.1024
	1.0	-9.8	-9.4	8.6	0.130		1.0	-6.5	-6.6	8.3	0.01
	2.0	-6.5	-6.4	0.0	0.005		2.0	-3.7	-3.6	0.0	0.0144
	3.0	-3.2	-3.4	9.4	0.048		3.0	-0.9	-0.6	9.7	0.1156
	4.0	0.1	-0.4	36.8	0.260		4.0	1.8	2.4	37.5	0.3136
R^2		-6.5	-12.4	90.0	0.866	R^2		-3.7	-9.6	90.1	0.556
					0.990						0.994
Eu	0.0	-8.1	-8.0	31.8	0.006	Ho	0.0	-7.1	-7.2	36.5	0.010
	1.0	-5.2	-5.0	7.0	0.048		1.0	-4.1	-4.2	9.2	0.005
	2.0	-2.4	-2.0	0.1	0.130		2.0	-1.2	-1.2	0.0	0.002
	3.0	0.5	1.0	11.3	0.250		3.0	1.8	1.8	8.8	0.000
	4.0	3.4	4.0	40.4	0.410		4.0	4.8	4.8	35.5	0.000
R^2		-2.4	-8.0	90.6	0.844	R^2		-1.2	-7.2	90.0	0.017
					0.991						1.000
Yb	0.0	-5.9	-6.0	36.5	0.010						
	1.0	-2.9	-3.0	9.2	0.005						
	2.0	0.0	0.0	0.0	0.002						
	3.0	3.0	3.0	8.8	0.000						
	4.0	6.0	6.0	35.5	0.000						
		0.0	-6.0	90.0	0.017						
					1.000						

Table B.7- log D and pH calculations for Cyanex 272 at 0.1 M concentration with TOPO at 0.01M concentration

Extractant	**Cyanex 272 +TOPO (Komatsu & Freiser, 1989)**					**Concentration**	**Cyanex 272 0.1 M +TOPO 0.01 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-8.9	-9.5	35.9	0.372	Pr	0.0	-8.6	-8.4	31.8	0.026
	1.0	-6.2	-6.5	8.9	0.090		1.0	-5.7	-5.4	7.0	0.068
	2.0	-3.5	-3.5	0.0	0.000		2.0	-2.8	-2.4	0.1	0.130
	3.0	-0.8	-0.5	9.1	0.102		3.0	0.1	0.6	11.3	0.212
	4.0	1.9	2.5	36.1	0.397		4.0	3.0	3.6	40.4	0.314
R^2		-3.5	-9.5	90.0	0.962	R^2		-2.8	-8.4	90.6	0.748
					0.989						0.992
Eu	0.0	-7.3	-7.6	40.2	0.090	Ho	0.0	-6.5	-6.5	38.9	0.000
	1.0	-4.3	-4.6	11.2	0.102		1.0	-3.4	-3.5	10.5	0.014
	2.0	-1.3	-1.6	0.1	0.116		2.0	-0.3	-0.5	0.1	0.058
	3.0	1.8	1.4	7.1	0.130		3.0	2.9	2.5	7.6	0.130
	4.0	4.8	4.4	32.0	0.144		4.0	6.0	5.5	33.2	0.230
R^2		-1.3	-7.6	90.6	0.582	R^2		-0.3	-6.5	90.3	0.432
					0.994						0.995
Yb	0.0	-4.8	-5.1	35.9	0.137						
	1.0	-1.9	-2.1	8.9	0.032						
	2.0	0.9	0.9	0.0	0.000						
	3.0	3.7	3.9	9.1	0.040						
	4.0	6.5	6.9	36.1	0.152						
		0.9	-5.1	90.0	0.362						
					0.996						

Table B.8- log D and pH calculations for Cyanex 272 at 0.1 M concentration

Extractant	**Cyanex 272+ with ClO4 (Komatsu & Freiser, 1989)**						**Concentration**			**0.1 M**
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-12.5	-12.0	33.1	0.281	Pr	0.0	-10.6	-10.3	35.0	0.116
	1.0	-9.4	-9.0	7.6	0.152		1.0	-7.5	-7.3	8.5	0.044
	2.0	-6.3	-6.0	0.1	0.062		2.0	-4.4	-4.3	0.0	0.006
	3.0	-3.1	-3.0	10.6	0.012		3.0	-1.3	-1.3	9.5	0.003
	4.0	0.0	0.0	39.1	0.001		4.0	1.9	1.7	37.0	0.032
R^2		-6.3	-12.0	90.3	0.508	R^2		-4.4	-10.3	90.0	0.201
					0.994						0.998
Eu	0.0	-8.9	-8.8	36.4	0.012	Ho	0.0	-6.7	-6.9	34.5	0.063
	1.0	-5.8	-5.8	9.2	0.002		1.0	-3.8	-3.9	8.2	0.004
	2.0	-2.8	-2.8	0.0	0.001		2.0	-1.0	-0.9	0.0	0.017
	3.0	0.3	0.2	8.8	0.010		3.0	1.8	2.1	9.8	0.102
	4.0	3.4	3.2	35.6	0.029		4.0	4.6	5.1	37.6	0.260
R^2		-2.8	-8.8	90.0	0.053	R^2		-1.0	-6.9	90.1	0.446
					0.999						0.995
Yb	0.0	-5.6	-6.0	38.1	0.137						
	1.0	-2.7	-3.0	10.0	0.073						
	2.0	0.2	0.0	0.0	0.029						
	3.0	3.1	3.0	8.0	0.005						
	4.0	6.0	6.0	34.0	0.001						
R^2		0.2	-6.0	90.1	0.245						
					0.997						

Table B.9- log D and pH calculations for TBDGA at 0.25 M concentration

Extractant	**TBDGA (D. F. Peppard et al., 1958)**					**Concentration**	**0.25 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-1.5	-1.5	39.7	0.002	Ce	0.0	-1.3	-1.3	34.0	0.000
	1.0	1.7	1.5	10.9	0.017		1.0	1.6	1.7	8.0	0.006
	2.0	4.8	4.5	0.1	0.090		2.0	4.6	4.7	0.0	0.029
	3.0	8.0	7.5	7.3	0.221		3.0	7.5	7.7	10.0	0.068
	4.0	11.2	10.5	32.5	0.410		4.0	10.4	10.7	38.1	0.123
R^2		4.8	-1.5	90.5	0.739	R^2		4.6	-1.3	90.1	0.225
					0.992						0.997
Pr	0.0	-1.2	-1.2	35.2	0.000	Nd	0.0	-1.2	-1.1	39.4	0.020
	1.0	1.7	1.8	8.6	0.001		1.0	2.0	1.9	10.8	0.005
	2.0	4.7	4.8	0.0	0.005		2.0	5.2	4.9	0.1	0.078
	3.0	7.7	7.8	9.4	0.012		3.0	8.4	7.9	7.4	0.240
	4.0	10.6	10.8	36.8	0.023		4.0	11.6	10.9	32.7	0.490
R^2		4.7	-1.2	90.0	0.041	R^2		5.2	-1.1	90.4	0.833
					1.000						0.991

Table B.10-Part A- log D and pH calculations for Cyanex 272 at 0.1 M concentration

Extractant		**Cyanex 272 (L. I. Deqian, 2017)**					**Concentration**	**0.1 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-10.1	-11.0	39.1	0.902	Ce	0.0	-8.9	-9.8	36.7	0.884
	1.0	-7.4	-8.0	10.6	0.360		1.0	-6.3	-6.8	9.4	0.250
	2.0	-4.8	-5.0	0.1	0.062		2.0	-3.7	-3.8	0.0	0.004
	3.0	-2.1	-2.0	7.6	0.010		3.0	-1.2	-0.8	8.6	0.144
	4.0	0.5	1.0	33.1	0.203		4.0	1.4	2.2	35.3	0.672
R^2		-4.8	-11.0	90.3	1.538	R^2		-3.7	-9.8	90.0	1.954
					0.983						0.978
Pr	0.0	-8.2	-9.2	36.0	1.000	Nd	0.0	-7.9	-7.2	17.9	0.456
	1.0	-5.7	-6.2	9.0	0.250		1.0	-5.4	-5.2	5.0	0.051
	2.0	-3.2	-3.2	0.0	0.000		2.0	-3.0	-3.2	0.1	0.051
	3.0	-0.7	-0.2	9.0	0.250		3.0	-0.5	-1.2	3.2	0.456
	4.0	1.8	2.8	36.0	1.000		4.0	1.9	0.8	14.3	1.266
R^2		-3.2	-9.2	90.0	2.500	R^2		-3.0	-7.2	40.3	2.278
					0.972						0.943
Sm	0.0	-7.9	-8.6	38.8	0.526	Eu	0.0	-7.7	-8.0	34.5	0.076
	1.0	-5.1	-5.6	10.4	0.226		1.0	-4.9	-5.0	8.3	0.006
	2.0	-2.4	-2.6	0.1	0.051		2.0	-2.1	-2.0	0.0	0.016
	3.0	0.4	0.4	7.7	0.001		3.0	0.7	1.0	9.8	0.106
	4.0	3.1	3.4	33.4	0.076		4.0	3.5	4.0	37.5	0.276
R^2		-2.4	-8.6	90.3	0.878	R^2		-2.1	-8.0	90.1	0.478

Table B.10-Part B- log D and pH calculations for Cyanex 272 at 0.1 M concentration

Extractant	**Cyanex 272 (L. I. Deqian, 2017)**					**Concentration**	**0.1 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Gd	0.0	-7.4	-8.0	36.1	0.366	Tb	0.0	-6.9	-7.5	36.0	0.360
	1.0	-4.7	-5.0	9.0	0.093		1.0	-4.2	-4.5	9.0	0.090
	2.0	-2.0	-2.0	0.0	0.000		2.0	-1.5	-1.5	0.0	0.000
	3.0	0.7	1.0	9.0	0.087		3.0	1.2	1.5	9.0	0.090
	4.0	3.4	4.0	35.9	0.354		4.0	3.9	4.5	36.0	0.360
R^2		-2.0	-8.0	90.0	0.900	R^2		-1.5	-7.5	90.0	0.900
Dy	0.0	-6.8	-7.3	40.1	0.303	Ho	0.0	-6.5	-7.2	39.4	0.456
	1.0	-3.7	-4.3	11.1	0.331		1.0	-3.7	-4.2	10.7	0.226
	2.0	-0.9	-1.3	0.1	0.141		2.0	-0.9	-1.2	0.1	0.076
	3.0	1.9	1.7	7.1	0.031		3.0	1.9	1.8	7.4	0.006
	4.0	4.7	4.7	32.1	0.001		4.0	4.7	4.8	32.8	0.016
R^2		-1.0	-7.3	90.5	0.805	R^2		-0.9	-7.2	90.4	0.778
					0.991						0.991
Er	0.0	-6.2	-6.8	37.8	0.422	Tm	0.0	-6.4	-6.4	36.0	0.000
	1.0	-3.4	-3.8	9.9	0.160		1.0	-3.4	-3.4	9.0	0.000
	2.0	-0.7	-0.8	0.0	0.022		2.0	-0.4	-0.4	0.0	0.000
	3.0	2.1	2.2	8.1	0.010		3.0	2.6	2.6	9.0	0.000
	4.0	4.9	5.2	34.2	0.123		4.0	5.6	5.6	36.0	0.000
R^2		-0.7	-6.8	90.1	0.737	R^2		-0.4	-6.4	90.0	0.000

Table B.10 -Part C- log D and pH calculations for Cyanex 272 at 0.1 M concentration

Extractant	**Cyanex 272 (L. I. Deqian, 2017)**					**Concentration**	**0.1 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Yb	0.0	-5.8	-5.8	34.7	0.008	Lu	0.0	-5.6	-5.8	35.4	0.063
	1.0	-2.9	-2.8	8.4	0.000		1.0	-2.7	-2.8	8.7	0.010
	2.0	0.0	0.2	0.0	0.012		2.0	0.2	0.2	0.0	0.002
	3.0	3.0	3.2	9.7	0.044		3.0	3.0	3.2	9.3	0.040
	4.0	5.9	6.2	37.3	0.096		4.0	5.9	6.2	36.6	0.123
R^2		0.0	-5.8	90.1	0.161	R^2		0.2	-5.8	90.0	0.237
					0.998						0.997
Y	0.0	-6.8	-6.6	32.2	0.051						
	1.0	-3.8	-3.6	7.2	0.076						
	2.0	-0.9	-0.6	0.1	0.106						
	3.0	2.1	2.5	11.1	0.141						
	4.0	5.0	5.5	40.0	0.181						
R^2		-0.9	-6.6	90.5	0.553						
					0.994						

Table B.11- log D and pH calculations for D2EHEPA

Extractant	**D2EHEPA (Chen et al., 2020)**					**Concentration**	**N/A**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-3.7	-4.1	34.6	0.122	Ce	0.0	-3.3	-3.8	37.2	0.206
	1.0	-1.0	-1.1	8.3	0.014		1.0	-0.5	-0.8	9.6	0.077
	2.0	1.8	1.9	0.0	0.013		2.0	2.4	2.3	0.0	0.010
	3.0	4.6	4.9	9.7	0.121		3.0	5.2	5.3	8.4	0.006
	4.0	7.3	7.9	37.4	0.337		4.0	8.0	8.3	34.8	0.063
R^2		1.8	-4.1	90.1	0.607	R^2		2.4	-3.8	90.1	0.363
					0.993						0.996
Nd	0.0	-2.6	-3.2	36.4	0.294	Pr	0.0	-1.2	-1.8	38.9	0.295
	1.0	0.1	-0.2	9.2	0.084		1.0	1.6	1.2	10.5	0.151
	2.0	2.9	2.9	0.0	0.001		2.0	4.5	4.2	0.1	0.055
	3.0	5.6	5.9	8.8	0.047		3.0	7.3	7.2	7.6	0.007
	4.0	8.4	8.9	35.6	0.220		4.0	10.1	10.2	33.2	0.005
R^2		2.9	-3.2	90.0	0.645	R^2		4.5	-1.8	90.3	0.514
					0.993						0.994

Table B.12- log D and pH calculations for DNPP at 0.2 concentration

Extractant		**DNPP (Anitha et al., 2014)**				**Concentration**			**0.2**		
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	1.2	1.0	36.5	0.032	Dy	0.0	2.8	3.0	36.1	0.044
	1.0	-1.9	-2.0	9.2	0.005		1.0	-0.1	0.0	9.1	0.012
	2.0	-5.0	-5.0	0.0	0.002		2.0	-3.0	-3.0	0.0	0.000
	3.0	-8.2	-8.0	8.8	0.023		3.0	-5.9	-6.0	8.9	0.008
	4.0	-11.3	-11.0	35.5	0.068		4.0	-8.8	-9.0	35.9	0.036
R^2		-5.0	1.0	90.0	0.129	R^2		-3.0	3.0	90.0	0.101
					0.999						0.999
Y	0.0	4.2	4.1	35.5	0.010						
	1.0	1.2	1.1	8.8	0.005						
	2.0	-1.9	-1.9	0.0	0.002						
	3.0	-4.9	-4.9	9.2	0.000						
	4.0	-7.9	-7.9	36.5	0.000						
R^2		-1.9	4.1	90.0	0.017						
					1.000						

Table B.13- log D and pH calculations for Cyanex 572

Extractant	**Cyanex 572 (Y. Wang et al., 2015)**					**Concentration**	**N/A**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ho	0.0	-1.1	-1.3	36.2	0.032	Er	0.0	-0.4	-0.6	36.2	0.046
	1.0	1.8	1.7	9.1	0.010		1.0	2.5	2.4	9.1	0.013
	2.0	4.7	4.7	0.0	0.000		2.0	5.4	5.4	0.0	0.000
	3.0	7.7	7.7	8.9	0.004		3.0	8.3	8.4	8.9	0.007
	4.0	10.6	10.7	35.8	0.020		4.0	11.2	11.4	35.8	0.034
R^2		4.7	-1.3	90.0	0.066	R^2		5.4	-0.6	90.0	0.101
					0.999						0.999
Tm	0.0	-0.6	-0.6	35.3	0.001	Yb	0.0	-0.5	-1.4	36.9	0.879
	1.0	2.4	2.4	8.6	0.000		1.0	2.1	1.6	9.5	0.258
	2.0	5.3	5.4	0.0	0.004		2.0	4.7	4.6	0.0	0.006
	3.0	8.3	8.4	9.4	0.013		3.0	7.2	7.6	8.5	0.124
	4.0	11.2	11.4	36.8	0.026		4.0	9.8	10.6	35.1	0.612
R^2		5.3	-0.6	90.0	0.045	R^2		4.7	-1.4	90.0	1.879
					1.000						0.979
Lu	0.0	0.0	0.9	35.3	0.766						
	1.0	3.4	3.9	8.7	0.216						
	2.0	6.8	6.9	0.0	0.003						
	3.0	10.2	9.9	9.3	0.126						
	4.0	13.6	12.9	36.7	0.585						

Table B.14- log D and pH calculations for HEHEMP at 0.1 M concentration

Extractant	**HEHEMP (Q. Zhao et al., 2019)**					**Concentration**	**0.1 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ho	0.0	-1.9	-2.3	36.0	0.176	Er	0.0	-1.6	-2.0	36.0	0.212
	1.0	0.9	0.7	9.0	0.044		1.0	1.2	1.0	9.0	0.053
	2.0	3.7	3.7	0.0	0.000		2.0	4.0	4.0	0.0	0.000
	3.0	6.5	6.7	9.0	0.044		3.0	6.8	7.0	9.0	0.053
	4.0	9.3	9.7	36.0	0.176		4.0	9.5	10.0	36.0	0.212
R^2		3.7	-2.3	90.0	0.441	R^2		4.0	-2.0	90.0	0.529
					0.995						0.994
Tm	0.0	-1.3	-1.4	35.0	0.010	Yb	0.0	-1.1	-1.3	35.8	0.058
	1.0	1.6	1.6	8.5	0.000		1.0	1.8	1.7	8.9	0.012
	2.0	4.5	4.6	0.0	0.006		2.0	4.6	4.7	0.0	0.000
	3.0	7.4	7.6	9.5	0.029		3.0	7.5	7.7	9.1	0.023
	4.0	10.3	10.6	37.0	0.068		4.0	10.4	10.7	36.2	0.078
R^2		4.5	-1.4	90.0	0.113	R^2		4.6	-1.3	90.0	0.171
					0.999						0.998
Lu	0.0	-1.0	-1.1	36.1	0.023						
	1.0	2.0	1.9	9.1	0.006						
	2.0	4.9	4.9	0.0	0.000						
	3.0	7.8	7.9	8.9	0.004						
	4.0	10.8	10.9	35.9	0.017						
R^2		4.9	-1.1	90.0	0.049						
					0.999						

Table B.15- log D and pH calculations for HL4 at 0.002 M concentration

Extractant	**HL4 (Y. Lu & Liao, 2016)**					**Concentration**	**0.002 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-2.9	-2.9	35.8	0.002	Pr	0.0	-2.3	-2.4	36.0	0.022
	1.0	-5.9	-5.9	8.9	0.001		1.0	-5.3	-5.4	9.0	0.005
	2.0	-8.9	-8.9	0.0	0.000		2.0	-8.4	-8.4	0.0	0.000
	3.0	-11.9	-11.9	9.1	0.000		3.0	-11.5	-11.4	9.0	0.006
	4.0	-14.9	-14.9	36.2	0.000		4.0	-14.6	-14.4	36.0	0.023
R^2		-8.9	-2.9	90.0	0.004	R^2		-8.4	-2.4	90.0	0.056
					1.000						0.999
Gd	0.0	-1.2	-1.4	35.9	0.044	Tb	0.0	-0.6	-0.8	36.1	0.038
	1.0	-4.3	-4.4	8.9	0.012		1.0	-3.7	-3.8	9.0	0.009
	2.0	-7.4	-7.4	0.0	0.000		2.0	-6.8	-6.8	0.0	0.000
	3.0	-10.5	-10.4	9.1	0.008		3.0	-9.9	-9.8	9.0	0.011
	4.0	-13.6	-13.4	36.1	0.036		4.0	-13.0	-12.8	35.9	0.042
R^2		-7.4	-1.4	90.0	0.101	R^2		-6.8	-0.8	90.0	0.100
					0.999						0.999
Yb	0.0	0.6	0.6	36.0	0.000	Lu	0.0	0.9	0.9	36.0	0.000
	1.0	-2.4	-2.4	9.0	0.000		1.0	-2.1	-2.1	9.0	0.000
	2.0	-5.4	-5.4	0.0	0.000		2.0	-5.1	-5.1	0.0	0.000
	3.0	-8.4	-8.4	9.0	0.000		3.0	-8.1	-8.1	9.0	0.000
	4.0	-11.4	-11.4	36.0	0.000		4.0	-11.1	-11.1	36.0	0.000
R^2		-5.4	0.6	90.0	0.000			-5.1	0.9	90.0	0.000
					1.000						1.000

Table B.16- log D and pH calculations for HEHAPP at 0.05 M concentration

Extractant	**HL4 (Y. Lu & Liao, 2016)**					**Concentration**	**0.05 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-1.8	-1.5	35.8	0.075	Gd	0.0	-1.2	-1.1	36.0	0.004
	1.0	-4.6	-4.5	8.9	0.016		1.0	-4.1	-4.1	9.0	0.001
	2.0	-7.5	-7.5	0.0	0.000		2.0	-7.1	-7.1	0.0	0.000
	3.0	-10.3	-10.5	9.1	0.028		3.0	-10.1	-10.1	9.0	0.001
	4.0	-13.2	-13.5	36.2	0.098		4.0	-13.0	-13.1	36.0	0.005
R^2		-7.5	-1.5	90.0	0.217	R^2		-7.1	-1.1	90.0	0.011
					0.998						1.000
Lu	0.0	1.9	1.4	35.6	0.253	Y	0.0	0.5	0.2	35.8	0.125
	1.0	-1.3	-1.6	8.8	0.073		1.0	-2.6	-2.8	8.9	0.035
	2.0	-4.6	-4.6	0.0	0.001		2.0	-5.8	-5.8	0.0	0.000
	3.0	-7.8	-7.6	9.2	0.039		3.0	-9.0	-8.8	9.1	0.022
	4.0	-11.0	-10.6	36.4	0.185		4.0	-12.1	-11.8	36.2	0.098
R^2		-4.6	1.4	90.0	0.551	R^2		-5.8	0.2	90.0	0.280
					0.994						0.997

Table B.17-Part A log D and pH calculations for Cekaonic Acid at 0.56 M concentration

Extractant	**Cekaonic Acid (Singh et al., 2006)**					**Concentration**	**0.56 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-13.9	-13.8	36.4	0.008	Ce	0.0	-13.2	-13.2	36.0	0.004
	1.0	-10.8	-10.8	9.2	0.001		1.0	-10.2	-10.2	9.0	0.001
	2.0	-7.7	-7.8	0.0	0.001		2.0	-7.2	-7.2	0.0	0.000
	3.0	-4.7	-4.8	8.8	0.008		3.0	-4.2	-4.2	9.0	0.001
	4.0	-1.6	-1.8	35.6	0.023		4.0	-1.1	-1.2	36.0	0.004
R^2		-7.7	-13.8	90.0	0.041	R^2		-7.2	-13.2	90.0	0.009
					1.000						1.000
Pr	0.0	-13.6	-13.4	35.8	0.068	Nd	0.0	-13.3	-13.1	36.1	0.017
	1.0	-10.5	-10.4	8.9	0.020		1.0	-10.2	-10.1	9.1	0.004
	2.0	-7.4	-7.4	0.0	0.000		2.0	-7.1	-7.1	0.0	0.000
	3.0	-4.3	-4.4	9.1	0.010		3.0	-4.0	-4.1	8.9	0.006
	4.0	-1.2	-1.4	36.2	0.048		4.0	-1.0	-1.1	35.9	0.022
R^2		-7.4	-13.4	90.0	0.146	R^2		-7.1	-13.1	90.0	0.049
					0.998						0.999
Sm	0.0	-13.1	-13.1	37.2	0.000	Gd	0.0	-13.2	-13.0	37.0	0.020
	1.0	-10.1	-10.1	9.6	0.002		1.0	-10.1	-10.0	9.5	0.001
	2.0	-7.0	-7.1	0.0	0.010		2.0	-6.9	-7.0	0.0	0.006
	3.0	-3.9	-4.1	8.4	0.026		3.0	-3.8	-4.0	8.5	0.036
	4.0	-0.9	-1.1	34.8	0.048		4.0	-0.7	-1.0	35.0	0.090
R^2		-7.0	-13.1	90.1	0.086			-6.9	-13.0	90.0	0.153
					0.999						0.998

Table B.17-Part B- log D and pH calculations for Cekaonic Acid at 0.56 M concentration

Extractant	**Cekaonic Acid (Singh et al., 2006)**					**Concentration**	**0.56 M**				
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Dy	0.0	-11.6	-12.0	35.4	0.221	Ho	0.0	-14.0	-13.4	36.6	0.423
	1.0	-8.8	-9.0	8.7	0.044		1.0	-10.7	-10.4	9.3	0.090
	2.0	-6.1	-6.0	0.0	0.003		2.0	-7.3	-7.4	0.0	0.002
	3.0	-3.3	-3.0	9.3	0.096		3.0	-4.0	-4.4	8.7	0.160
	4.0	-0.6	0.0	36.6	0.325		4.0	-0.6	-1.4	35.4	0.563
R^2		-6.1	-12.0	90.0	0.688	R^2		-7.3	-13.4	90.0	1.238
					0.992						0.986
Y	0.0	-13.8	-13.6	36.6	0.053						
	1.0	-10.6	-10.6	9.3	0.008						
	2.0	-7.5	-7.6	0.0	0.003						
	3.0	-4.4	-4.6	8.7	0.036						
	4.0	-1.2	-1.6	35.4	0.109						
R^2		-7.5	-13.6	90.0	0.209						
					0.998						

Table B.18-Part A- log D and pH calculations for Neo heptanol at 0.73 M concentration

Extractant	**Neo heptanol (Singh et al., 2006)**					**Concentration**	**0.73 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-13.9	-14.6	38.1	0.504	Pr	0.0	-15.1	-15.0	37.1	0.003
	1.0	-11.2	-11.6	10.0	0.194		1.0	-12.0	-12.0	9.5	0.000
	2.0	-8.4	-8.6	0.0	0.029		2.0	-9.0	-9.0	0.0	0.008
	3.0	-5.7	-5.6	8.0	0.010		3.0	-5.9	-6.0	8.5	0.026
	4.0	-3.0	-2.6	34.0	0.137		4.0	-2.8	-3.0	34.9	0.053
R^2		-8.4	-14.6	90.1	0.873	R^2		-9.0	-15.0	90.0	0.089
					0.990						0.999
Nd	0.0	-13.9	-14.2	35.5	0.058	Sm	0.0	-14.0	-14.1	35.3	0.002
	1.0	-11.1	-11.2	8.8	0.010		1.0	-11.1	-11.1	8.6	0.000
	2.0	-8.2	-8.2	0.0	0.002		2.0	-8.1	-8.1	0.0	0.004
	3.0	-5.3	-5.2	9.2	0.032		3.0	-5.2	-5.1	9.4	0.012
	4.0	-2.5	-2.2	36.5	0.102		4.0	-2.2	-2.1	36.7	0.026
R^2		-8.2	-14.2	90.0	0.204	R^2		-8.1	-14.1	90.0	0.043
					0.998						1.000
Gd	0.0	-15.4	-15.0	34.7	0.168	Dy	0.0	-14.4	-14.1	35.6	0.109
	1.0	-12.3	-12.0	8.4	0.068		1.0	-11.3	-11.1	8.8	0.032
	2.0	-9.1	-9.0	0.0	0.012		2.0	-8.1	-8.1	0.0	0.001
	3.0	-6.0	-6.0	9.7	0.002		3.0	-5.0	-5.1	9.2	0.014
	4.0	-2.8	-3.0	37.3	0.036		4.0	-1.8	-2.1	36.4	0.073
R^2		-9.1	-15.0	90.1	0.286			-8.1	-14.1	90.0	0.229
					0.997						0.997

Table B.18-Part B- log D and pH calculations for Neo Heptanic Acid at 0.73 M concentration

Extractant	**Neo heptanol (Singh et al., 2006)**					**Concentration**	**0.73 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ho	0.0	-13.1	-13.3	35.5	0.026	Y	0.0	-13.0	-13.2	34.2	0.053
	1.0	-10.2	-10.3	8.8	0.004		1.0	-10.2	-10.2	8.1	0.002
	2.0	-7.3	-7.3	0.0	0.002		2.0	-7.4	-7.2	0.0	0.023
	3.0	-4.4	-4.3	9.2	0.020		3.0	-4.5	-4.2	9.9	0.116
	4.0	-1.5	-1.3	36.5	0.058		4.0	-1.7	-1.2	37.8	0.281
R^2		-7.3	-13.3	90.0	0.108	R^2		-7.4	-13.2	90.1	0.474
					0.999						0.995

Table B.19-Part A- log D and pH calculations for Cyanex 301 at 0.2 M concentration

Extractant	**Cyanex 301 (M. L. P. Reddy et al., 1999)**					**Concentration**	**0.2 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-6.2	-6.4	35.9	0.019	Nd	0.0	-5.7	-5.8	35.9	0.018
	1.0	-9.3	-9.4	8.9	0.006		1.0	-8.8	-8.8	8.9	0.005
	2.0	-12.3	-12.4	0.0	0.000		2.0	-11.8	-11.8	0.0	0.000
	3.0	-15.4	-15.4	9.1	0.003		3.0	-14.9	-14.8	9.1	0.003
	4.0	-18.5	-18.4	36.2	0.013		4.0	-17.9	-17.8	36.1	0.013
R^2		-12.3	-6.4	90.0	0.040	R^2		-11.8	-5.8	90.0	0.039
					1.000						1.000

Table B.19-Part B- log D and pH calculations for Cyanex 301 at 0.2 M concentration

Extractant	**Cyanex 301 (M. L. P. Reddy et al., 1999)**					**Concentration**	**0.2 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Eu	0.0	-4.7	-4.7	36.0	0.000	Tb	0.0	-3.4	-3.5	35.9	0.018
	1.0	-7.7	-7.7	9.0	0.000		1.0	-6.5	-6.5	8.9	0.005
	2.0	-10.7	-10.7	0.0	0.000		2.0	-9.5	-9.5	0.0	0.000
	3.0	-13.7	-13.7	9.0	0.000		3.0	-12.6	-12.5	9.1	0.003
	4.0	-16.7	-16.7	36.0	0.000		4.0	-15.6	-15.5	36.1	0.013
R^2		-10.7	-4.7	90.0	0.000	R^2		-9.5	-3.5	90.0	0.039
					1.000						1.000
Tm	0.0	-1.9	-1.9	36.0	0.000	Ho	0.0	-2.6	-2.6	36.0	0.000
	1.0	-4.9	-4.9	9.0	0.000		1.0	-5.6	-5.6	9.0	0.000
	2.0	-7.9	-7.9	0.0	0.000		2.0	-8.6	-8.6	0.0	0.000
	3.0	-10.9	-10.9	9.0	0.000		3.0	-11.6	-11.6	9.0	0.000
	4.0	-13.9	-13.9	36.0	0.000		4.0	-14.6	-14.6	36.0	0.000
R^2		-7.9	-1.9	90.0	0.000	R^2		-8.6	-2.6	90.0	0.000
					1.000						1.000
Lu	0.0	-1.5	-1.5	36.0	0.000	Y	0.0	-2.4	-2.6	36.0	0.015
	1.0	-4.5	-4.5	9.0	0.000		1.0	-5.5	-5.6	9.0	0.004
	2.0	-7.5	-7.5	0.0	0.000		2.0	-8.6	-8.6	0.0	0.000
	3.0	-10.5	-10.5	9.0	0.000		3.0	-11.6	-11.6	9.0	0.004
	4.0	-13.5	-13.5	36.0	0.000		4.0	-14.7	-14.6	36.0	0.016
R^2		-7.5	-1.5	90.0	0.000			-8.6	-2.6	90.0	0.039
					1.000						1.000

Table B.20- log D and pH calculations for HEDHP at 0.04 M Concentration and HEH/EHP at 0.06 M concentration

Extractant	**HEDHP and HEH/EHP (Zhang et al., 2008)**						**Concentration**	**0.04M**		
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	-6.2	-6.5	37.0	0.078	Nd	0.0	-4.6	-4.7	35.9	0.009
	1.0	-3.3	-3.5	9.5	0.032		1.0	-1.7	-1.7	9.0	0.002
	2.0	-0.4	-0.5	0.0	0.006		2.0	1.3	1.3	0.0	0.000
	3.0	2.5	2.5	8.5	0.000		3.0	4.2	4.3	9.0	0.003
	4.0	5.4	5.5	35.0	0.014		4.0	7.2	7.3	36.1	0.011
R^2		-0.4	-6.5	90.0	0.132	R^2		1.3	-4.7	90.0	0.025
					0.999						1.000
Sm	0.0	-3.6	-3.9	36.0	0.090	Gd	0.0	-2.7	-3.3	33.9	0.331
	1.0	-0.8	-0.9	9.0	0.023		1.0	-0.1	-0.3	8.0	0.040
	2.0	2.1	2.1	0.0	0.000		2.0	2.5	2.7	0.0	0.031
	3.0	5.0	5.1	9.0	0.022		3.0	5.2	5.7	10.1	0.303
	4.0	7.8	8.1	36.0	0.090		4.0	7.8	8.7	38.1	0.856
R^2		2.1	-3.9	90.0	0.225	R^2		2.5	-3.3	90.2	1.559
					0.998						0.983

Table B.21-Part A- log D and pH calculations for EHEPA

Extractant	**EHEPA+D2EHPA (Registered et al., 2007)**					**Concentration**				**N/A**
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Pr	0.0	-6.2	-6.1	36.0	0.009	Nd	0.0	-6.0	-5.9	36.0	0.002
	1.0	-3.1	-3.1	9.0	0.002		1.0	-2.9	-2.9	9.0	0.000
	2.0	-0.1	-0.1	0.0	0.000		2.0	0.1	0.1	0.0	0.000
	3.0	3.0	2.9	9.0	0.003		3.0	3.1	3.1	9.0	0.001
	4.0	6.0	5.9	36.0	0.011		4.0	6.1	6.1	36.0	0.003
R^2		-0.1	-6.1	90.0	0.025	R^2		0.1	-5.9	90.0	0.006
					1.000						1.000
Sm	0.0	-4.9	-4.9	36.2	0.004	Eu	0.0	-4.5	-4.5	36.2	0.000
	1.0	-1.9	-1.9	9.1	0.000		1.0	-1.5	-1.5	9.1	0.000
	2.0	1.2	1.1	0.0	0.000		2.0	1.5	1.5	0.0	0.000
	3.0	4.2	4.1	8.9	0.004		3.0	4.5	4.5	8.9	0.001
	4.0	7.2	7.1	35.8	0.010		4.0	7.5	7.5	35.8	0.001
R^2		1.2	-4.9	90.0	0.018	R^2		1.5	-4.5	90.0	0.002
					1.000						1.000
Gd	0.0	-4.4	-4.2	35.8	0.018	Ho	0.0	-3.0	-2.9	36.5	0.006
	1.0	-1.3	-1.2	8.9	0.006		1.0	0.0	0.1	9.2	0.000
	2.0	1.7	1.8	0.0	0.000		2.0	3.1	3.1	0.0	0.002
	3.0	4.8	4.8	9.1	0.002		3.0	6.2	6.1	8.8	0.010
	4.0	7.9	7.8	36.2	0.011		4.0	9.2	9.1	35.5	0.026
R^2		1.7	-4.2	90.0	0.037			3.1	-2.9	90.0	0.044
					1.000						1.000

Table B.21-Part B- log D and pH calculations for EHEPA

Extractant		**EHEPA+D2EHPA (Registered et al., 2007)**				**Concentration**		**N/A**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Er	0.0	-2.6	-2.6	36.2	0.000	Y	0.0	-2.8	-2.8	36.0	0.000
	1.0	0.4	0.4	9.1	0.000		1.0	0.3	0.3	9.0	0.000
	2.0	3.4	3.4	0.0	0.000		2.0	3.3	3.3	0.0	0.000
	3.0	6.4	6.4	8.9	0.002		3.0	6.3	6.3	9.0	0.000
	4.0	9.4	9.4	35.8	0.004		4.0	9.3	9.3	36.0	0.000
R^2		3.4	-2.6	90.0	0.006	R^2		3.3	-2.8	90.0	0.000
					1.000						1.000

Table B.22-Part A- log D and pH calculations for P227 at 0.16 M concentration

Extractant		**P227 (Chen et al., 2020)**				**Concentration**		**0.16 M**			
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ho	0.0	-3.0	-3.5	36.2	0.238	Er	0.0	-2.7	-3.2	35.8	0.235
	1.0	-0.2	-0.5	9.1	0.064		1.0	0.0	-0.2	8.9	0.055
	2.0	2.5	2.5	0.0	0.000		2.0	2.8	2.8	0.0	0.000
	3.0	5.3	5.5	8.9	0.047		3.0	5.5	5.8	9.1	0.070
	4.0	8.0	8.5	35.8	0.204		4.0	8.3	8.8	36.2	0.265
R^2		2.5	-3.5	90.0	0.554	R^2		2.8	-3.2	90.0	0.626
					0.994						0.993

Table B.22-Part B- log D and pH calculations for P227 at 0.16 M concentration

Extractant	**P227 (Chen et al., 2020)**					**Concentration**					**0.16 M**
REE	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**pH**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Tm	0.0	-2.4	-2.9	36.1	0.260	Yb	0.0	-2.2	-2.4	35.9	0.029
	1.0	0.4	0.1	9.1	0.068		1.0	0.7	0.6	9.0	0.007
	2.0	3.2	3.1	0.0	0.000		2.0	3.6	3.6	0.0	0.000
	3.0	5.9	6.1	8.9	0.058		3.0	6.5	6.6	9.0	0.009
	4.0	8.7	9.1	35.9	0.240		4.0	9.5	9.6	36.1	0.032
R^2		3.2	-2.9	90.0	0.626	R^2		3.6	-2.4	90.0	0.077
					0.993						0.999
Lu	0.0	-2.1	-1.9	36.1	0.027	Y	0.0	-2.7	-3.4	35.9	0.439
	1.0	1.0	1.1	9.1	0.006		1.0	-0.1	-0.4	8.9	0.106
	2.0	4.1	4.1	0.0	0.000		2.0	2.6	2.6	0.0	0.000
	3.0	7.2	7.1	8.9	0.010		3.0	5.3	5.6	9.1	0.122
	4.0	10.3	10.1	35.9	0.034		4.0	7.9	8.6	36.2	0.473
R^2		4.1	-1.9	90.0	0.077	R^2		2.6	-3.4	90.0	1.140
					0.999						0.987

APPENDIX C

Table C.1-Part A-The intercept difference between two adjacent rare earth elements

No	REE	1	2	3	4	5	6	7
1	La-Ce			-1.07	-0.37			
2	Ce-Pr	-0.24	-0.30	0.63	-0.10	-0.36		
3	Pr-Nd	-0.18	-0.23	-0.47	-0.20	-0.31		
4	Nd-Pm							
5	Pm-Sm							
6	Sm-Eu							
7	Eu-Gd							
8	Gd-Tb							
9	Tb-Dy	-0.35						
10	Dy-Ho	-0.30						
11	Ho-Er	-0.40			-0.48			
12	Er-Tm			-0.41				
13	Tm-Yb							
14	Yb-Lu	-0.18						

Table C.1-Part B- The intercept difference between two adjacent rare earth elements

No	REE	8	9	10	11	12	13	14
1	La-Ce		-0.20	-1.20	-0.33			-1.00
2	Ce-Pr		-0.04	-0.60	-0.60			
3	Pr-Nd		-0.16		-1.37			
4	Nd-Pm							
5	Pm-Sm							
6	Sm-Eu							
7	Eu-Gd			-0.02				
8	Gd-Tb			-0.48				
9	Tb-Dy			-0.20				
10	Dy-Ho			-0.10				
11	Ho-Er			-0.40			-0.70	-0.32
12	Er-Tm			-0.40			0.00	-0.50
13	Tm-Yb			-0.56			0.80	-0.15
14	Yb-Lu			-0.04			-2.30	-0.36

Table C.1-Part C- The intercept difference between two adjacent rare earth elements

No	REE	15	16	17	18	19	20	21	22
1	La-Ce			-0.58					
2	Ce-Pr			0.18					
3	Pr-Nd			-0.24	-0.89			-0.15	
4	Nd-Pm				-0.10				
5	Pm-Sm								
6	Sm-Eu							-0.36	
7	Eu-Gd							-0.26	
8	Gd-Tb	-0.56							
9	Tb-Dy								
10	Dy-Ho			1.25	-0.80				
11	Ho-Er							-0.32	-0.29
12	Er-Tm								-0.35
13	Tm-Yb								-0.50
14	Yb-Lu	-0.35							-0.44

Table C.2-A brief statically analysis for the intercept difference between two adjacent rare earth elements

No	X	X-mean	(X-mean)^2	No	X	X-mean	(X-mean)^2	No	X	X-mean	(X-mean)^2
1	-0.2400	0.1084	0.0117	21	-0.1600	0.1884	0.0355	41	-0.1500	0.1984	0.0394
2	-0.1800	0.1684	0.0284	22	-1.2000	-0.8516	0.7253	42	-0.3600	-0.0116	0.0001
3	-0.3500	-0.0016	0.0000	23	-0.6000	-0.2516	0.0633	43	-0.5600	-0.2116	0.0448
4	-0.3000	0.0484	0.0023	24	-0.0200	0.3284	0.1078	44	-0.3497	-0.0013	0.0000
5	-0.4000	-0.0516	0.0027	25	-0.4800	-0.1316	0.0173	45	-0.5800	-0.2316	0.0536
6	-0.1800	0.1684	0.0284	26	-0.2000	0.1484	0.0220	46	0.1800	0.5284	0.2792
7	-0.3000	0.0484	0.0023	27	-0.1000	0.2484	0.0617	47	-0.2400	0.1084	0.0117
8	-0.2300	0.1184	0.0140	28	-0.4000	-0.0516	0.0027	48	1.2500	1.5984	2.5548
9	-1.0700	-0.7216	0.5207	29	-0.4000	-0.0516	0.0027	49	--0.8900	-0.5416	0.2934
10	0.6321	0.9805	0.9613	30	-0.5600	-0.2116	0.0448	50	-0.8000	-0.4516	0.2040
11	-0.4711	-0.1227	0.0151	31	-0.0400	0.3084	0.0951	51	-0.1500	0.1984	0.0394
12	-0.4100	-0.0616	0.0038	32	-0.3300	0.0184	0.0003	52	-0.3590	-0.0106	0.0001
13	-0.3700	-0.0216	0.0005	33	-0.6000	-0.2516	0.0633	53	-0.2610	0.0874	0.0076
14	-0.0990	0.2494	0.0622	34	-1.3700	-1.0216	1.0437	54	-0.3200	0.0284	0.0008
15	-0.2010	0.1474	0.0217	35	-0.7000	-0.3516	0.1236	55	-0.2900	0.0584	0.0034
16	-0.4771	-0.1287	0.0166	36	0.0000	0.3484	0.1214	56	-0.3500	-0.0016	0.0000
17	-0.3600	-0.0116	0.0001	37	0.8000	1.1484	1.3188	57	-0.5000	-0.1516	0.0230
18	-0.3100	0.0384	0.0015	38	-2.3000	-1.9516	3.8088	58	-0.4400	-0.0916	0.0084
19	-0.2000	0.1484	0.0220	39	-0.3200	0.0284	0.0008				
20	-0.0400	0.3084	0.0951	40	-0.5000	-0.1516	0.0230				

APPENDIX D

Table D.1-Part A Relation between log D and log (H_2R_2) for HEDHP

Solvent Extractant		**HEDHP**		**pH**	**1.3**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R2**	**Model 1**		
						Intercept	**Model**	**Error**
							1.85	0.11
1	La						2.20	
2	Ce						2.55	
3	Pr						2.90	
4	Nd	$logD = 2.9125\log(H_2R_2) + 3.4175$ (Zhang et al., 2008)	0.999	$logD = 3\log(H_2R_2) + 3.25$ (Zhang et al., 2008)	0.999	3.25 (Zhang et al., 2008)		
							3.24	0.01
5	Pm						3.59	
6	Sm	$logD = 2.9200\log(H_2R_2) + 3.9760$ (Zhang et al., 2008)	0.999	$logD = 3\log(H_2R_2) + 3.82$ (Zhang et al., 2008)	0.999	3.82 (Zhang et al., 2008)		
							3.94	0.12
7	Eu						4.29	
8	Gd	$logD = 3.1425\log(H_2R_2) + 4.5365$ (Zhang et al., 2008)	0.994	$logD = 3\log(H_2R_2) + 4.83$ (Zhang et al., 2008)	0.994	4.83 (Zhang et al., 2008)		
							4.64	0.19

Table D.1-Part B Relation between log D and log (H_2R_2) for HEDHP

Solvent Extractant		**HEDHP**		**pH**	**1.3**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R2**	**Model 1**		
						Intercept	**Model**	**Eror**
							1.85	0.11
9	Tb						4.99	
10	Dy						5.33	
11	Ho						5.68	
12	Er						6.03	
13	Tm						6.38	
14	Yb						6.73	
15	Lu						7.08	
16	Y						5.83	

Table D.2- Relation between log D and log (H_2R_2) for HEH/EHP

Solvent Extractant		**HEH/EHP**		**pH**	**1.9**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**Error**
							2.28	0.08
1	La	$logD = 3.095\log(H_2R_2) + 2.5310$ (Zhang et al., 2008)	0.999	$logD = 3\log(H_2R_2) + 2.7$ (Zhang et al., 2008)	0.999	2.72 (Zhang et al., 2008)	2.63	0.09
2	Ce						2.98	
3	Pr						3.33	
4	Nd						3.67	
5	Pm						4.02	
6	Sm	$logD = 3.200\log(H_2R_2) + 3.9975$ (Zhang et al., 2008)	0.999	$logD = 3\log(H_2R_2) + 4.4$ (Zhang et al., 2008)	0.996	4.38 (Zhang et al., 2008)	4.37	0.01
7	Eu						4.72	
8	Gd	$logD = 3.135\log(H_2R_2) + 4.9280$ (Zhang et al., 2008)	0.999	$logD = 3\log(H_2R_2) + 5.2$ (Zhang et al., 2008)	0.998	5.22 (Zhang et al., 2008)	5.07	0.15
9	Tb						5.42	
10	Dy						5.76	
11	Ho						6.11	
12	Er						6.46	
13	Tm						6.81	
14	Yb						7.16	
15	Lu						7.51	
16	Y						6.26	

Table D.3-Part A Relation between log D and log (H_2R_2) for HEHEHP

Solvent Extractant		**HEHEHP**		**pH**	**N/A**			
No	**RE E**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**Eror r**
							-4.50	0.61
1	La						-4.15	
2	Ce						-3.80	
3	Pr						-3.45	
4	Nd						-3.11	
5	Pm						-2.76	
6	Sm						-2.41	
7	Eu						-2.06	
8	Gd						-1.71	

Table D.3-Part B Relation between log D and log (H_2R_2) for HEHEHP

Solvent Extractant		**HEHEHP**		**pH**		**N/A**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**		**R^2**	**Model 1**		
							Intercept	**Model**	**Error**
								-4.50	0.61
9	Tb							-1.36	
10	Dy							-1.02	
11	Ho	$logD = 1.8300\log(H_2R_2) + 1.4188$ (Q. Zhao et al., 2019)	0.994	$logD = 2\log(H_2R_2) + 1.07$	(Q. Zhao et al., 2019)	0.999	-0.90 (Q. Zhao et al., 2019)	-0.67	0.23
12	Er	$logD = 1.7220\log(H_2R_2) + 1.0550$ (Q. Zhao et al., 2019)	0.999	$logD = 2\log(H_2R_2) + 0.49$	(Q. Zhao et al., 2019)	0.999	0.40 (Q. Zhao et al., 2019)	-0.32	0.72
13	Tm	$logD = 1.7100\log(H_2R_2) + 0.7712$ (Q. Zhao et al., 2019)	0.999	$logD = 2\log(H_2R_2) + 0.22$	(Q. Zhao et al., 2019)	0.999	0.20 (Q. Zhao et al., 2019)	0.03	0.17
14	Yb	$logD = 1.8000\log(H_2R_2) + 0.7150$ (Q. Zhao et al., 2019)	0.999	$logD = 2\log(H_2R_2) + 0.35$	(Q. Zhao et al., 2019)	0.999	0.50 (Q. Zhao et al., 2019)	0.38	0.12
15	Lu	$logD = 2.0175\log(H_2R_2) + 0.8675$ (Q. Zhao et al., 2019)	0.999	$logD = 2\log(H_2R_2) + 0.87$	(Q. Zhao et al., 2019)	0.999	1.10 (Q. Zhao et al., 2019)	0.73	0.37
16	Y	$logD = 2.1435\log(H_2R_2) + 1.2195$ (Q. Zhao et al., 2019)	1.000	$logD = 2\log(H_2R_2) + 1.51$	(Q. Zhao et al., 2019)	0.999	1.51 (Q. Zhao et al., 2019)	-0.52	2.03

Table D.4- Relation between log D and log (H_2R_2) for Cyanex 272

Solvent Extractant		**Cyanex 272**		**pH**		**N/A**		
No	**REE**	**log D vs log (H_2R_2) (Experimental)**	**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**	**R^2**	**Model 1**		
						Intercept	**Model**	**Error**
							-3.00	0.27
1	La						-2.65	
2	Ce						-2.30	
3	Pr						-1.95	
4	Nd						-1.61	
5	Pm						-1.26	
6	Sm						-0.91	
7	Eu	$logD = 3\log(H_2R_2) - 0.225$ (Inaba et al., 1993)	1.000	$logD = 3\,og(H_2R_2) - 0.225$ (Inaba et al., 1993)	1.000	-0.23 (Inaba et al., 1993)	-0.56	0.34
8	Gd						-0.21	
9	Tb	$logD = 3\log(H_2R_2) + 0.400$ (Inaba et al., 1993)	1.000	$logD = 3\,og(H_2R_2) + 0.400$ (Inaba et al., 1993)	1.000	0.40 (Inaba et al., 1993)	0.14	0.26
10	Dy						0.48	
11	Ho	$logD = 3\log(H_2R_2) + 0.800$ (Inaba et al., 1993)	1.000	$logD = 3\,og(H_2R_2) + 0.800$ (Inaba et al., 1993)	1.000	0.75 (Inaba et al., 1993)	0.83	0.08
12	Er						1.18	
13	Tm						1.53	
14	Yb	$logD = 3\log(H_2R_2) + 1.500$ (Inaba et al., 1993)	1.000	$logD = 3\,og(H_2R_2) + 1.500$ (Inaba et al., 1993)	1.000	1.50 (Inaba et al., 1993)	1.88	0.38
15	Lu						2.23	
16	Y						0.98	

Table D.5- Relation between log D and log (H_2R_2) for D2EHEPA

Solvent Extractant		**D2EHEPA**			**pH**		**N/A**			
No	**REE**	**log D vs log (H_2R_2) (Experimental)**		**R^2**	**log D vs log (H_2R_2) (Curve Fitting)**		**R^2**	**Model 1**		
								Intercept	**Model**	**Error**
									-3.90	0.35
1	La								-3.55	
2	Ce								-3.20	
3	Pr								-2.85	
4	Nd								-2.51	
5	Pm								-2.16	
6	Sm								-1.81	
7	Eu								-1.46	
8	Gd								-1.11	
9	Tb	$logD = 1.8723\log(H_2R_2) - 0.7071$	(S. Wu et al., 2017)	0.939	$logD = 2\log(H_2R_2) - 1.01$	(S. Wu et al., 2017)	0.996	-1.01 (S. Wu et al., 2017)	-0.76	0.25
10	Dy	$logD = 2.1291\log(H_2R_2) - 0.1375$	(S. Wu et al., 2017)	0.939	$logD = 2\log(H_2R_2) + 0.13$	(S. Wu et al., 2017)	0.996	0.13 (S. Wu et al., 2017)	-0.42	0.55
11	Ho								-0.07	
12	Er								0.28	
13	Tm								0.63	
14	Yb								0.98	
15	Lu								1.33	
16	Y	$logD = 1.9546\log(H_2R_2) + 0.4115$	(S. Wu et al., 2017)	0.939	$logD = 2\log(H_2R_2) + 0.32$	(S. Wu et al., 2017)	0.996	0.32 (S. Wu et al., 2017)	0.08	0.24

APPENDIX E

Table E.1-Part A- log D and log (H_2R_2) calculations for EHEHPA

Extractant	**EHEHPA (Registered et al., 2007)**			**pH**		**N/A**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**	
Pr	0.0	-1.3	-1.3	36.0	0.000	Nd	0.0	-1.0	-1.0	36.0	0.000
	1.0	1.8	1.8	9.0	0.000		1.0	2.0	2.0	9.0	0.000
	2.0	4.8	4.8	0.0	0.000		2.0	5.0	5.0	0.0	0.000
	3.0	7.8	7.8	9.0	0.000		3.0	8.0	8.0	9.0	0.000
	4.0	10.8	10.8	36.0	0.000		4.0	11.0	11.0	36.0	0.000
R^2		4.8	-1.3	90.0	0.000	R^2		5.0	-1.0	90.0	0.000
					1.000						1.000
Sm	0.0	0.1	0.1	36.0	0.000	Eu	0.0	0.3	0.3	36.6	0.000
	1.0	3.1	3.1	9.0	0.000		1.0	3.4	3.3	9.3	0.001
	2.0	6.1	6.1	0.0	0.000		2.0	6.4	6.3	0.0	0.002
	3.0	9.1	9.1	9.0	0.000		3.0	9.4	9.3	8.7	0.006
	4.0	12.1	12.1	36.0	0.000		4.0	12.4	12.3	35.4	0.010
R^2		6.1	0.1	90.0	0.000	R^2		6.4	0.3	90.0	0.019
					1.000						1.000
Gd	0.0	0.6	0.6	35.4	0.000	Ho	0.0	2.0	2.0	36.0	0.000
	1.0	3.6	3.6	8.7	0.001		1.0	5.0	5.0	9.0	0.000
	2.0	6.6	6.6	0.0	0.002		2.0	8.0	8.0	0.0	0.000
	3.0	9.6	9.6	9.3	0.006		3.0	11.0	11.0	9.0	0.000
	4.0	12.5	12.6	36.6	0.010		4.0	14.0	14.0	36.0	0.000
R^2		6.6	0.6	90.0	0.019			8.0	2.0	90.0	0.000
					1.000						1.000

Table E.1-Part B- log D and log (H_2R_2) calculations for EHEHPA

Extractant	**EHEHPA (Registered et al., 2007)**		**pH**			**N/A**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**	
Er	0.0	2.4	2.4	36.6	0.000	Y	0.0	2.2	2.2	36.0	0.000
	1.0	5.5	5.4	9.3	0.001		1.0	5.2	5.2	9.0	0.000
	2.0	8.5	8.4	0.0	0.002		2.0	8.2	8.2	0.0	0.000
	3.0	11.5	11.4	8.7	0.006		3.0	11.2	11.2	9.0	0.000
	4.0	14.5	14.4	35.4	0.010		4.0	14.2	14.2	36.0	0.000
R^2		8.5	2.4	90.0	0.019	R^2		8.2	2.2	90.0	0.000
					1.000						1.000

Table E.2-Part A- log D and log (H_2R_2) calculations for HEDHP

Extractant	**HEDHP (Zhang et al., 2008)**		**pH**			**1.3**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**	
Nd	0.0	3.4	3.3	35.9	0.028	Sm	0.0	4.0	3.8	36.0	0.024
	1.0	6.3	6.3	9.0	0.006		1.0	6.9	6.8	9.0	0.006
	2.0	9.2	9.3	0.0	0.000		2.0	9.8	9.8	0.0	0.000
	3.0	12.2	12.3	9.0	0.009		3.0	12.7	12.8	9.0	0.007
	4.0	15.1	15.3	36.1	0.033		4.0	15.7	15.8	36.0	0.027
R^2		9.2	3.3	90.0	0.077	R^2		9.8	3.8	90.0	0.064
					0.999						0.999

Table E.2-Part B- log D and log (H_2R_2) calculations for HEDHP

Extractant	**HEDHP (Zhang et al., 2008)**				**Concentration**	**1.3**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**	
Gd	0.0	4.5	4.8	35.9	0.086					
	1.0	7.7	7.8	8.9	0.023					
	2.0	10.8	10.8	0.0	0.000					
	3.0	14.0	13.8	9.1	0.018					
	4.0	17.1	16.8	36.1	0.076					
R^2		10.8	4.8	90.0	0.203					
					0.998					

Table E.3-Part A- log D and log (H_2R_2) calculations for HEH/EHP

Extractant	**HEH/EHP (Zhang et al., 2008)**				**pH**		**1.9**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**		
La	0.0	2.5	2.7	36.0	0.036	Sm	0.0	4.0	4.4	36.2	0.146
	1.0	5.6	5.7	9.0	0.009		1.0	7.2	7.4	9.1	0.033
	2.0	8.7	8.7	0.0	0.000		2.0	10.4	10.4	0.0	0.000
	3.0	11.8	11.7	9.0	0.008		3.0	13.6	13.4	8.9	0.047
	4.0	14.9	14.7	36.0	0.033		4.0	16.8	16.4	35.8	0.174
R^2		8.7	2.7	90.0	0.086	R^2		10.4	4.4	90.0	0.402
					0.999						0.996

Table E.3-Part B- log D and log (H_2R_2) calculations for HEH/EHP

Extractant	**HEH/EHP (Zhang et al., 2008)**		**pH**		**1.9**
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Gd	0.0	4.9	5.2	35.7	0.085
	1.0	8.1	8.2	8.9	0.025
	2.0	11.2	11.2	0.0	0.000
	3.0	14.3	14.2	9.1	0.013
	4.0	17.5	17.2	36.3	0.062
R^2		11.2	5.2	90.0	0.185
					0.998

Table E.4-Part A- log D and log (H_2R_2) calculations for HEHEHP

Extractant	**HEHEHP (Q. Zhao et al., 2019)**		**pH**		**N/A**					
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Ho	0.0	-0.9	-0.9	16.2	0.000	Er	0.0	0.8	0.4	16.6	0.176
	1.0	1.1	1.1	4.1	0.000		1.0	2.6	2.4	4.3	0.063
	2.0	3.2	3.1	0.0	0.001		2.0	4.4	4.4	0.0	0.006
	3.0	5.2	5.1	3.9	0.001		3.0	6.3	6.4	3.7	0.008
	4.0	7.2	7.1	15.8	0.002		4.0	8.1	8.4	15.4	0.068
R^2		3.2	-0.9	40.0	0.004	R^2		4.4	0.4	40.0	0.321
					1.000						0.992

Table E.4-Part B- log D and log (H_2R_2) calculations for HEHEHP

Extractant	**HEHEHP (Q. Zhao et al., 2019)**			**pH**		**N/A**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**	
Tm	0.0	0.8	0.2	15.8	0.304	Yb	0.0	1.1	0.5	16.1	0.319
	1.0	2.5	2.2	3.9	0.068		1.0	2.8	2.5	4.0	0.082
	2.0	4.2	4.2	0.0	0.001		2.0	4.5	4.5	0.0	0.000
	3.0	5.9	6.2	4.1	0.101		3.0	6.2	6.5	4.0	0.072
	4.0	7.6	8.2	16.2	0.370		4.0	7.9	8.5	15.9	0.299
R^2		4.2	0.2	40.0	0.845	R^2		4.5	0.5	40.0	0.773
					0.979						0.981
Lu	0.0	1.4	1.1	16.1	0.122	Y	0.0	1.2	1.5	16.0	0.084
	1.0	3.2	3.1	4.0	0.032		1.0	3.4	3.5	4.0	0.022
	2.0	5.1	5.1	0.0	0.000		2.0	5.5	5.5	0.0	0.000
	3.0	6.9	7.1	4.0	0.026		3.0	7.7	7.5	4.0	0.020
	4.0	8.7	9.1	15.9	0.110		4.0	9.8	9.5	16.0	0.080
R^2		5.1	1.1	40.0	0.289	R^2		5.5	1.5	40.0	0.206
					0.993						0.995

Table E.5- log D and log (H_2R_2) calculations for Cyanex 272

Extractant	**Cyanex 272 (Inaba et al., 1993)**			**pH**		**N/A**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Eu	0.0	-0.2	-0.2	36.0	0.000	Tb	0.0	0.4	0.4	36.0	0.000
	1.0	2.8	2.8	9.0	0.000		1.0	3.4	3.4	9.0	0.000
	2.0	5.8	5.8	0.0	0.000		2.0	6.4	6.4	0.0	0.000
	3.0	8.8	8.8	9.0	0.000		3.0	9.4	9.4	9.0	0.000
	4.0	11.8	11.8	36.0	0.000		4.0	12.4	12.4	36.0	0.000
R^2		5.8	-0.2	90.0	0.000	R^2		6.4	0.4	90.0	0.000
					1.000						1.000
Ho	0.0	0.8	0.8	36.0	0.000	Yb	0.0	1.5	1.5	36.0	0.000
	1.0	3.8	3.8	9.0	0.000		1.0	4.5	4.5	9.0	0.000
	2.0	6.8	6.8	0.0	0.000		2.0	7.5	7.5	0.0	0.000
	3.0	9.8	9.8	9.0	0.000		3.0	10.5	10.5	9.0	0.000
	4.0	12.8	12.8	36.0	0.000		4.0	13.5	13.5	36.0	0.000
R^2		6.8	0.8	90.0	0.000	R^2		7.5	1.5	90.0	0.000
					1.000						1.000

Table E.6- log D and log (H_2R_2) calculations for D2EHEPA

Extractant	**D2EHEPA (S. Wu et al., 2017)**			**pH**		**N/A**				
REE	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**			**REE**	**log(H_2R_2)**	**Log D_{Ex}**	**Log $D_{G=3}$**		
Tb	0.0	-0.7	-1.0	16.4	0.092	Dy	0.0	-0.1	0.1	15.9	0.072
	1.0	1.2	1.0	4.2	0.031		1.0	2.0	2.1	4.0	0.019
	2.0	3.0	3.0	0.0	0.002		2.0	4.1	4.1	0.0	0.000
	3.0	4.9	5.0	3.8	0.006		3.0	6.2	6.1	4.0	0.014
	4.0	6.8	7.0	15.6	0.043		4.0	8.4	8.1	16.1	0.062
R^2		3.0	-1.0	40.0	0.174	R^2		4.1	0.1	40.0	0.167
					0.996						0.996
Y	0.0	0.4	0.3	16.0	0.008						
	1.0	2.4	2.3	4.0	0.002						
	2.0	4.3	4.3	0.0	0.000						
	3.0	6.3	6.3	4.0	0.002						
	4.0	8.2	8.3	16.0	0.008						
R^2		4.3	0.3	40.0	0.021						
					0.999						

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